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Third Edition

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15

Modern Techniques in Fertilizer Application[1]

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Techniques of fertilizer application have changed markedly through the years. Increases in rates of fertilizer application, crop area fertilized, and farm size created the need for larger and faster application methods. In addition, the fertilizer industry has had to meet the needs of the growers as they change their farm operations. Such major changes as reduced tillage, increased irrigation, foliar application, and fertilizer-pesticide combinations have contributed greatly to changes in the fertilizer industry. Improvements and changes in fertilizer materials have also necessitated changes in application techniques. In this chapter, we describe some of the modern techniques being used in fertilizer application, how these techniques may affect fertilizer efficiency, and some changes in application methods needed to meet the agronomic and economic requirements of the future.

I. NEED FOR IMPROVED TECHNIQUES

A. Fertilizer Efficiency

A major goal of many agronomists and crop producers alike is to improve fertilizer efficiency. In other words, the goal is to produce greater crop yield per unit of fertilizer applied. Economists have predicted that fer-

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tilizer will undoubtedly become more expensive in the future due to escalating costs of natural gas, labor, mining, exploration, processing, and transportation. Some projections indicate that fertilizer prices will increase at a faster rate than crop commodity prices. Since these increased fertilizer costs are passed onto farmers, it becomes important for them to maximize fertilizer efficiency and, thus, increase profit.

New, modern application techniques provide an opportunity to increase fertilizer efficiency. For instance, applicators that will inject or band all fertilizer materials into the soil may play a significant role in conservation tillage systems. More precise metering and application of fertilizer through irrigation systems will surely improve fertilizer efficiency in irrigated, coarse-textured soils. In many cases, though, adoption of these new techniques will require modification of application equipment, new application equipment, or both, along with more intensive management by the farmer and the fertilizer dealer.

B. Environmental Considerations

Concern is being continually registered by the public toward the impact of fertilizers on the environment. Modern application techniques can play a significant role in preserving the quality of the environment while still producing optimum crop yields. For instance, subsurface application of P will significantly reduce the runoff of orthophosphate from no-till corn (*Zea mays* L.). Improved N application techniques by either timing or placement can markedly reduce the potential nitrate (NO_3^-) contamination of waters. Techniques to reduce environmental concern almost always result in improved fertilizer efficiency.

C. Time and Energy Considerations

Farmers are continually striving to reduce the time and energy expenditures necessary for maximum economic yield. Fertilizer suppliers are also trying to increase the pace of their operations while reducing the energy needed. Changes in application technique, such as bulk spreading of urea or urea–ammonium nitrate (UAN) mixtures, have allowed both the farmer and the supplier to gain time and energy efficiencies. However, some of these techniques that reduce the time and energy needed for application may not and often do not result in improved fertilizer efficiency or reduced environmental concern. Thus, the challenge is to maximize efficiency and minimize environmental concern while reducing time and energy needs, which necessitates the development of improved application equipment and techniques.

II. FERTILIZER EFFICIENCY AS INFLUENCED BY APPLICATION METHODS

Broadly, three objectives are involved in fertilizer placement. These are (i) to result in efficient fertilizer use by the plant, (ii) to prevent fertilizer salt injury to plants, and (iii) to provide an economical and convenient operation. The achievement of these objectives is determined to a large extent by certain general principles, summarized as follows:

1. Soil conditions (pH, texture, cation exchange capacity [CEC], organic matter content, bulk density, moisture, temperature, chemical content) will to a large extent govern fertilizer efficiency, that is, once a fertilizer has been added to soil, it reacts in and with soil to varying degrees as influenced primarily by the above soil factors.
2. Fertilizers have inherent chemical and physical properties that influence the degree to which they react in and with soil, such as the molecular form of a nutrient (ammonium [NH_4^+] vs. NO_3^-), chemically prepared polynutrient fertilizer (ammonium phosphate [$(NH_4)_2HPO_4$]), or a physical blend of mononutrient fertilizers (ammonium nitrate + potassium chloride + calcium phosphate [$NH_4NO_3 + KCl + Ca(H_2PO_4)_2$]), and particle size.
3. Plants take up nutrients dissolved in the soil solution largely by diffusion and mass flow and to a lesser extent from direct contact of a root with mineral or organic nutrient–containing materials.
4. The absolute amount of nutrients taken up by the plant at any one time depends on (i) the size of the plant, that is, its root system (the larger the root system, the more surface area there is to absorb nutrients and the more contact there is between soil and plant); (ii) the amount of nutrient in the soil in a form that can be extracted by plant roots; and (iii) the temperature of both soil and air. Plant metabolism is directly related to temperature. At low temperature, metabolism is greatly reduced and nutrient uptake is slow.

The challenge is how to effectively manipulate or manage these principles to do the best job of achieving the objectives of fertilizer placement under a given set of conditions. The given conditions may include such factors as the crop to be grown, variety of the crop, field to be used, cultural practices to be used, and availability of capital for investment in the crop enterprise. Before a decision on fertilization can be made, definitive information on the soil in a particular field is needed: Is it of uniform type? What are the physical and chemical characteristics of the rooting zone? What is the fertility level? Soil testing is certainly an important practice to use to obtain this latter information. A more rational decision can be made concerning fertilizer and lime usage on the basis of soil test results. Such results provide information pertinent to the first principle discussed—soil conditions.

Eventually a method of fertilizer placement must be chosen. Whether the fertilizer is broadcast and plowed down, applied in the row, deep banded, foliar applied, or is applied using some combination of these methods depends on the set of conditions. What were the soil test results for pH, P, and K? What is the soil microclimate? Is fertility being built or maintained? Is the soil acid or alkaline, and to what degree? What is the root system of the crop grown—taproot or lateral? What volume of soil will the roots contact? What is the potential for surface runoff? What fertilizer materials are available? What are their physical and chemical characteristics? What kind of equipment is available for spreading? What is the price

Table 15–1. Location and method of fertilizer placement.

Location of placement	Method of placement
Surface	Broadcast
	Stripped
	Sidedressed
	Irrigation
Subsurface	Broadcast, plowed under
	Broadcast, disked in
	Sidedressed
	Row application with seed
	Banded apart from seed
	Irrigation
Directly onto plant	Foliar sprays

of fertilizer? The final decision often reflects the various degrees of influence of the specific given set of conditions.

Basically, all fertilizers are applied either to the soil surface or under the surface. (Only a few situations exist in which they are applied directly to the plant.) Several methods are used to make surface or subsurface application. Many management systems often combine these methods. Application methods are outlined in Table 15–1. In terms of the nature of placement involved, these methods can be generally considered as either *broadcast* or *banded*.

A. Band Versus Broadcast Placement

To more clearly understand the advantages and disadvantages associated with either banding or broadcasting fertilizers, a clear understanding of how fertilizer nutrients react when placed with soil is helpful. Because of these reactions, the method of placement is often dependent on the nature of the nutrient source and the crop being grown.

1. Nitrogen

Nitrogen is commonly added in the NH_4^+, ammonia (NH_3), NO_3^- or urea chemical forms. It is utilized by plants as NO_3^- or NH_4^+. Commonly used fertilizer forms of these sources are readily soluble in the soil solution. The non-NO_3^- forms are subject to biological oxidation to NO_3^- in well-drained soils. The NO_3^- form, being an anion and thus unreactive with the cation exchange complex of soil, is readily mobile in the soil solution and moves primarily vertically as soil water moves. Thus, placement of such a mobile ion is related primarily to its effect on row spacing, germination, seedling damage, and potential losses. When NH_4^+ is added to soil, it initially reacts with the cation exchange complex to become adsorbed to the surface of clay particles. Thus, mobility is diminished and uptake by the plant is restricted largely to absorption of solution NH_4^+, which is in equilibrium with that of the exchange complex. However, during the portion of the annual season that soil conditions are favorable for aerobic biologic activity, most available soil NH_4^+ will be transformed to the mobile form, NO_3^-.

Ammonia is applied as a pressurized liquid that immediately vaporizes as the liquid emerges from the applicator. For this reason, placement of NH_3 has to be made subsurface to prevent loss of the NH_3 vapor to the atmosphere. The NH_3 readily reacts in the soil with the exchange complex or water to form NH_4^+, which subsequently undergoes biologic oxidation to NO_3^-. A method sometimes used is the *cold flow method*, whereby NH_3 is supercooled to liquid form and metered into soil ahead of an incorporating implement.

Urea, being nonionic, must be transformed to NH_4^+ before it is available for plant use. This reaction readily takes place in warm moist soil in the presence of the naturally occurring enzyme urease to form ammonium carbonate [$(NH_4)_2CO_3$]. Unless a placement method is used to incorporate urea into the soil or unless there is sufficient moisture for it to be readily moved into the soil, there is potential risk for losses of N, since $(NH_4)_2CO_3$ readily breaks down to NH_3, which can be lost to the atmosphere, especially in an alkaline medium. Losses due to this mechanism can be sizeable (Fenn & Miyamoto, 1981; Fenn et al., 1981a, 1981b). Since high concentrations of NH_3 can accumulate in the zone of urea hydrolysis, care must be taken to minimize risk of root toxicity by using low rates of urea, banding it away from the row, or diluting the NH_3 accumulation by broadcasting and incorporating. Creamer and Fox (1980) reported NH_4^+ toxicity resulting from band applications of urea or diammonium phosphate (DAP) and concluded that plant toxic accumulations of NH_3 occur near band applications of urea in all except very acid soils. They also reported that cool temperature (10 vs. 20° C) lowered nitrification of NH_4^+ enough to result in NH_3 persisting around the hydrolysis zone for longer periods of time. The NH_4^+ formed from hydrolysis of urea undergoes biologic oxidation to NO_3^- just as that from any other NH_4^+ source.

2. Phosphorus

Phosphorus is commonly applied in the orthomolecular form (PO_4^{3-}), polymolecular form, or mineral form (apatite). However, the ortho-form is primarily used. Dependent on the associated molecular cation and the degree to which the three negative charges of the orthophosphate anion are saturated by the associated cation, solubility of orthophosphatic fertilizer salts can widely vary. Also, soluble orthophosphate in soil reacts rapidly with cations, hydrous oxide coatings, or cations in solution to form reaction products of varying solubility. Since P is absorbed by plants as $H_2PO_4^-$ or HPO_4^{2-}, it is these ionic forms that need to be present in the soil solution for the plant to utilize it. The degree to which soil P reactions take place and the reaction products formed are related largely to soil pH and to relative amounts of precipitating cations on soil particle surfaces or in soil solution. Even so, orthophosphates react rapidly when added to most agricultural soils to form compounds much less soluble—and therefore less available to the plant—than of the ortho-salt added. This greatly reduces the efficiency of fertilizer P added to the crop being grown in that particular year. Hence, placement of such a material is of considerable importance.

Availability of orthophosphate is related to the solubility of the salt used and to the chemical nature of the soil to which the salts are added. By broadcasting with a water-soluble salt, solubility effects can be partially modified by the particle size of the salt added (Engelstad & Terman, 1966). The larger the particle size, the less contact the salt has with soil; consequently, due to dissolution rate of the salt, a sphere containing a greater concentration of soluble P than that from finely divided particles is maintained. These spheres of soluble P then exist as potential feeding sites for plant roots as they penetrate throughout the soil. Banding soluble phosphatic salts results in a similar effect.

From a placement standpoint with respect to P, the objective is to restrict contact of the added soluble salt with soil to realize greater efficiency of the material by reducing phosphate fixation. Even under best conditions, no more than 20 to 30% of added P is likely to be taken up by a crop during the first growing season after addition of the fertilizer.

Since P is so immobile in soil, it must be placed in such a way that plant roots will come in contact with it. Physiologically, P stimulates early root proliferation of seedlings, which directly affects growth rate (dry matter accumulation) of the plant. This early growth stimulation usually results in higher yields of short-season crops and of full-season crops grown in locations where length of growing season is marginal for such crops. For this reason, it is of special importance that P be placed in such manner that as seedling roots grow, they come in contact with the fertilizer. This implies a band or row application of a soluble P salt. The amount to be applied in this manner depends on the level of plant-available P present in the particular soil. In soils low in P saturation (high P fixation capacity), soluble P added will be utilized more efficiently from a band placement method as long as the band is located in such position that plant roots contact it. If broadcast applications of soluble P are made on such soils, granulated fertilizers will be more efficient than pulverized fertilizers due to the solubility pattern previously explained.

If insoluble forms of P (e.g., phosphate rock [apatite]) are used, it should be placed in such a way as to enhance reaction (maximize contact with soil). Enhancement can be accomplished by increasing the surface area of the material (finely ground) and adding it to the soil in such a way as to maximize contact (broadcast and disk in). For this reason, efficiency of insoluble phosphates can be increased by using finely ground material and thoroughly mixing them in the soil. This effectively increases P solubility of such materials in the soil, that is, the resultant reaction products are more soluble than the material added.

One point that should be made here is the interaction between N and P. Evidence has been accumulated to show that P efficiency is improved by adding it with N. For example, the reason DAP has been shown in some experiments to be more efficient than superphosphate is thought to be due to the presence of NH_4^+ at the same fertilizer site with P. Band application of phosphatic fertilizers has been thoroughly reviewed by Richards (1977), and this publication is recommended for those desiring more information on the topic.

3. Potassium

Potassium is commonly applied to soil as soluble Cl^-, sulfate (SO_4^{2-}), or nitrate salts. Upon dissolution in the soil solution, K exists as the cation K^+, which reacts with the soil cation exchange complex to become relatively immobile. The K^+ ion can also react at interlayer exchange sites of expanded clay particles and become fixed or unavailable to plants. Most added K^+, however, is likely to become adsorbed to cation exchange surfaces and become available for plant use from solution and by contact exchange. The important aspect of K fertilization with respect to placement is that it is relatively immobile and does not react in most cases to become unavailable to plants; therefore, there is no consistent effect of placement on efficient plant utilization of added K^+. As a soluble salt, however, it can contribute to salt injury during germination and seedling growth. For this reason, care must be taken when a seed-salt contact placement is being used. For the same reason, when large amounts are being used, placement should be made to minimize salt damage (band away from seed or broadcast).

4. Secondary Nutrients

The secondary elements Ca and Mg are slightly mobile in the soil. Calcium and Mg attach to the exchange complex of the soil and act much like K. Plant uptake mechanisms are also similar to K. Dolomitic lime, a common source for both Ca and Mg, is usually broadcast-applied because of the higher application rates often needed to reduce soil acidity. Gypsum ($CaSO_4$) also provides Ca and is generally broadcast-applied. Magnesium can be supplied as potassium-magnesium sulfate ($K_2SO_4 \cdot 2\,MgSO_4$) and is also broadcast applied. However, row applications of Mg to shallow-rooted crops such as potatoes (*Solanum tuberosum* L.) are sometimes more efficient.

Sulfur in the SO_4^{2-} form is quite mobile and is usually broadcast-applied as gypsum or elemental S. The elemental S is oxidized to the SO_4^{2-} form, which is the form taken up by plants. Special instances occur where it is desirable to localize or band-place the S fertilizer. Liquid formulations of S, such as ammonium thiosulfate [$(NH_4)_2S_2O_3$], are becoming more frequently added to liquid fertilizers for band placement to row crops. Highly acidic or acid-forming compounds of S (e.g., sulfuric acid [H_2SO_4] and ferrous sulfate [$FeSO_4$]) are sometimes band-applied to highly calcareous soils where acidification of a band or small soil area within the plant rooting zone is necessary.

5. Micronutrients

Micronutrient fertilization is quite complex due to the many different forms of micronutrients available, the crop management system, and the uptake mechanisms and specific needs of the crop. As a result application methods vary widely. Soluble nutrients, such as B, and the sulfate sources of Zn, Cu, and Mn are often broadcast on the soil surface. The more insol-

uble sources are added as solid compounds or in some suspended form to the macronutrient carriers that are either solid, liquid, or suspension grades. Relatively expensive materials are generally banded to row crops for economical reasons. On the other hand, specific micronutrient needs of intensive, high-value citrus (*Citrus* spp.) and vegetable crops are usually met through broadcast, foliar applications. When the micronutrient is applied with the macronutrient, the application method is usually determined by the nature and relative efficiency of the macronutrient rather than the micronutrient. An example is the common introduction of relatively small amounts of micronutrients into banded starter fertilizers (see section IIC2). Murphy and Walsh (1972) provide a detailed discussion of the fertilizer sources and the application methods used to provide improved efficiency of each of the micronutrients.

B. Dual Placement of Nitrogen and Phosphorus

Considerable attention has been given in recent years to simultaneously injecting anhydrous NH_3 and liquid $(NH_4)_2HPO_4$ solutions in a band 10 to 15 cm below the surface. Subsequent tillage after this dual placement does not disturb these bands; thus, the practice allows for once-over, preplant fertilization with the band advantage for phosphate efficiency and the added advantage for phosphate efficiency of having N and P at the same site. Use of anhydrous NH_3 also gives an economical advantage to this practice. Much of the developmental work for this practice has been conducted by Murphy (1981) and Leikam et al. (1979) in Kansas. Their results show significant advantage from preplant dual application on yield and P uptake on low P soils. Their work has shown the increased P uptake to be related to use of NH_4^+ and that it was necessary for NH_4^+ and P to be in the same soil retention zone to obtain best results.

Lamond and Moyer (1983) found in Kansas trials on soils testing low to medium in P that knifed (subsurface band) fertilization of UAN potassium tripolyphosphate (0–11–21 [0–25–25]) or ammonium polyphosphate (10–15–0 [10–34–0]), and KCl (0–0–50 [0–0–60]) significantly increased tall fescue (*Festuca arundinacea* Schreb.) yields, N content, and N, P, and K uptake compared with surface broadcast fertilization. Higher N uptake indicated higher availability and recovery of N, possibly due to less N volatilization, reduced N tie-up by soil microorganisms, or both. When forage yields were averaged across all fertilizer treatments, the knifed method of application increased yields by 9% in one experiment and 24% in the other.

Wisconsin data (Fixen & Wolkowski, 1981) compared dual N-P placement of anhydrous NH_3 and ammonium polyphosphate with a 5 by 5 cm band placement of N-P for corn grown on a Plano (fine-silty, mixed, mesic Typic Argiudolls) silt loam in 1980 and 1981. Little advantage was shown for the dual N-P application over the conventionally used N-P starter in a 5 by 5 cm band.

The dual N-P application concept was summarized in Nebraska by Penas (1981). He indicated the practice has been found to work best with

wheat (*Triticum aestivum* L.) and that the preplant application should be made in a 25- to 50-cm band spacing, with a 30- to 38-cm spacing being ideal.

C. Time of Application

The time at which fertilizer is applied does not always show a direct cause and effect relationship between fertilizer efficiency and method of application. However, the trend toward large farming operations of 300 to 1000 ha that may require seedbed preparation and planting in a relatively short period of time has placed increased emphasis on applying fertilizer prior to the annual spring planting rush. The fertilizer industry has also shown much interest in this as an attempt to spread out their distribution season in such a manner as to minimize shortage of local fertilizer supplies due to transportation problems usually encountered during the rush spring season.

Apart from the convenience and economics usually associated with the purchase and application of fertilizers 8 to 30 weeks ahead of an intended crop, consideration should largely be given to climatic factors involved, mobility of the fertilizer nutrients to be applied, and soil test levels of nutrients.

1. Climatic Factors

Soil temperature, soil moisture content, and air temperature should also be considered in determining when to apply fertilizers. Perhaps the climatic effect of greatest concern is the effect of temperature on nitrification. As previously mentioned, NH_4^+ will react with soil strongly enough to withstand leaching. However, nitrifying bacteria in soil oxidize NH_4^+ to NO_3^-, in which form it is subject to potential loss either by leaching or denitrification. The rate of nitrification is temperature dependent, being almost static at the freezing point, but increasing to the point that at around 10° C the conversion rate is considered to be rapid. To lower the risk of leaching or denitrification losses, one must not apply N so far ahead of need by the crop that losses would likely be encountered. For this reason, fall application of N for corn is a risky practice except for climatic areas where air and soil temperatures are low enough by late fall or early winter that nitrification is negligible and where they stay that low until late winter or early spring. The middle and northern Corn Belt is the largest N-using area where this practice can feasibly be used. Fall application to coarse-textured soils even under these cold conditions is still not recommended due to the high leaching potential. Injection of anhydrous NH_3 to normal depths of 15 to 25 cm also represents a mechanism to delay nitrification since soil temperature at such depths is cooler than at the surface. The highly concentrated NH_3 band is also sufficient to delay rapid conversion to NO_3^- by temporarily inhibiting the nitrifying organisms.

In recent years, nitrification inhibitors have been developed and are commercially available for use as additives to N fertilizers as a means of

suppressing nitrification by decreasing activity of the nitrifying bacteria *Nitrosomonas*. Reports from their use indicate greatest advantage when used on soils that have a substantial potential for denitrification during spring and early summer.

2. *Mobility of Fertilizer Nutrients*

Since the immobile fertilizer nutrients move such short distances from the soil-fertilizer reaction zone, plant uptake can be insufficient in soils cool enough in the rooting zone to delay root growth and thus reduce the area of absorbing root surfaces. Band or seed placement is often used in such soils to help overcome low mobility. Phosphorus and, to a lesser extent, K are the nutrients most often used in this manner. A small amount is applied in the row or in a band at the time of planting to improve early start of seedlings and is therefore called *starter fertilizer*.

3. *Soil Test Levels*

At high soil test levels, it would generally be immaterial as to when fertilizer is applied. In fact, at high soil test levels, fertilizers may not even be justified on an annual cost-and-return basis except for those who place value on maintaining soil test levels in the high range. However, at low soil test levels of the immobile nutrients, rates normally recommended for broadcasting can be reduced 50% if banded. Banding, of course, usually implies application near the row at planting, meaning that if the lower rates made possible by banding are to be used application would not be done until planting.

D. Residual Nutrient Level

When residual nutrient levels in soil have been built to or naturally occur at high levels, little agronomic growth or yield response can be expected from further application of the fertilizer nutrient being considered. Thus, under these soil test conditions, the method of fertilizer application is generally of little significance.

High residual nutrient levels have received considerable attention since the mid-1970s and was the subject of a special symposium held during the 1981 annual meetings of the American Society of Agronomy. During this symposium, Cope and Khasawneh (1981) reported that there has been a general and often substantial increase in residual soil test levels of P and K in the USA during recent years. Crop response data from field studies in the southeastern, midwestern, and western U.S. states consistently showed little or no yield increase to application of P and K to soils testing high or above (Parks et al., 1981; Randall, 1981b; Westfall, 1981). Parks and Walker (1969) also reported from field studies with corn that as residual soil levels of K increase, the effect of band placement of fertilizer K decreases. Cope (1981) reported on extensive, long-term residual soil test studies conducted in Alabama with several crops and showed that P-K rates that gave the highest economic returns also resulted in increased re-

sidual soil test values. Further, such increased residual levels occurred despite annual crop removal values often exceeding economically optimum P-K rates. Olson et al. (1982) reported on a comprehensive 8-yr field study conducted on four major soils in Nebraska with corn. Treatments tested at each site were fertilizer recommendations made by five soil testing laboratories on the basis of either cation balance, nutrient replacement, or nutrient sufficiency philosophies. Despite large differences in amount and kinds of fertilizers recommended on the basis of these three philosophies, no differences in yield were obtained. These results substantiate use of the nutrient sufficiency philosophy both agronomically and economically when the rate of fertilizer to use at a given residual nutrient level is determined.

Peaslee (1978) reported on field studies conducted in Kentucky to determine P fertilizer rates necessary to get near maximum yields at various residual levels of available soil P. His results, shown in Table 15–2 and Fig. 15–1 and 15–2 show that at Bray and Kurtz no. 1 P extraction levels > 44 kg/ha, no further growth response from corn, soybeans [*Glycine max* (L.) Merr.], alfalfa (*Medicago sativa* L.), or clover (*Trifolium* spp.)–grass was obtained.

A commonly followed rule regarding band and broadcast rates of P is that where a P response is likely (low residual soil P, cool soil tempera-

Table 15-2. Effect of residual soil test P level on fertilizer P rates for near-maximum yields (Peaslee, 1978).

Bray and Kurtz no. 1 P level	Fertilizer P required for 0.95 maximum yield			
	Corn	Soybeans	Alfalfa	Clover-grass
kg/ha	kg/ha per year			
0	55	35	62	47
6	45	27	55	40
11	37	17	42	32
22	25	6	27	12
33	12	--	12	--
44	--	--	--	--

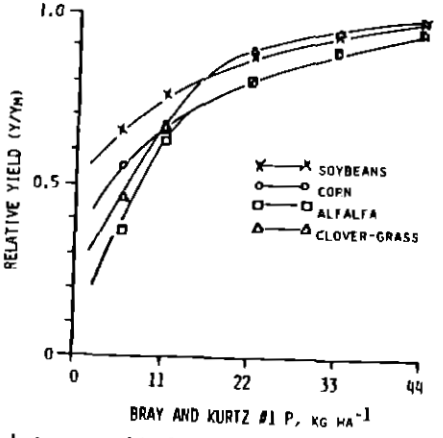

Fig. 15–1. Relationship between residual soil test P levels and relative yield of corn, soybeans, alfalfa, and grass-clover (Peaslee, 1978).

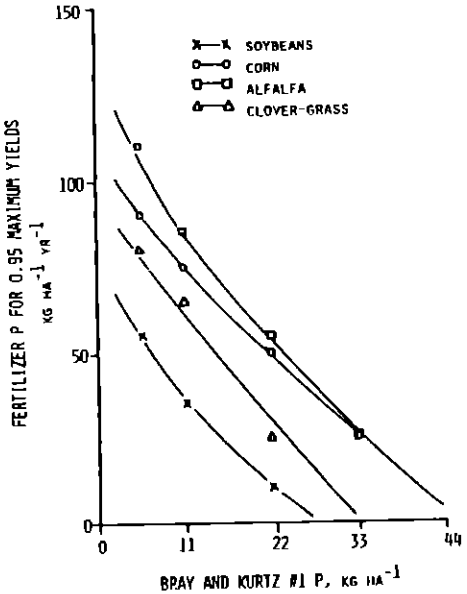

Fig. 15–2. Relationship between residual soil test P levels and fertilizer P required for near-maximum crop yields (Peaslee, 1978).

tures, or both), an economic efficiency can be obtained by banding fertilizer P; banded P is generally considered to be 1.5 to 2 times more effective than broadcast P (i.e., P rates can be cut by one-third to one-half if banded). A Nebraska study on winter wheat was recently reported by Peterson et al. (1981) to test this practice, which they reported to be popular in the High Plains area of Nebraska. After testing several rates of P applied either broadcast or drilled in the row with the seed, they concluded that the relative efficiency of band vs. broadcast P varied with residual soil P levels (Table 15–3). For low-testing soils the relative efficiency of banded P was about 3:1 compared with broadcast P, whereas for medium-testing soils the relative efficiency ratio was 1:1. Figure 15–3 shows the relationship they found between amounts of row and broadcast rates of fertilizer P required for equal yields of winter wheat grown at various residual soil P levels.

The effect of climate on band vs. broadcast P at various residual soil P levels can be seen in contrasting the Nebraska data cited above to results from dryland spring wheat studies in North Dakota (Alessi & Power, 1980). They conducted a comprehensive study for 6 yr by banding 15 kg P/ha per year on either previously unfertilized plots or on plots that had initially received 20, 40, 80, or 160 kg P/ha broadcast. Results indicated that wheat yields were increased from use of the banded 15 kg P/ha per year of all levels of residual P found in their study. Consequently, they concluded that banded P for spring wheat production in the cool spring climate of the Northern Great Plains was justified.

Similar results were reported from a field study conducted in Ontario (Sheard, 1980). This study was conducted to test the effect of banded P ei-

Table 15–3. Comparison of broadcast and row applied fertilizer P at different soil test residual P levels on winter wheat yields (Peterson et al., 1981).

Bray and Kurtz no. 1 P level	Calculated fertilizer P rates		Ratio of row to broadcast
	Broadcast for maximum yield	Row application for same yield as broadcast	
kg/ha	kg P/ha		
18	37	12	0.32
22	45	28	0.62
31	45	30	0.67
38	NS†	NS	1.00
43	NS	NS	1.00
43	27	22	0.82

† No significant difference between broadcast and row rates.

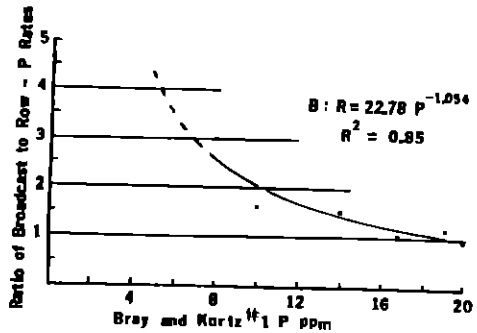

Fig. 15–3. Relationship of soil test P level and the ratio of broadcast and row P fertilizer rates required to obtain an equal grain yield response (Peterson et al., 1981).

ther alone or in the presence of ammonium-N (NH_4^+-N) or nitrate-N (NO_3^--N) on establishment of forage species. Results showed as much as a fivefold increase in seedling growth with up to 30 kg P/ha regardless of the forage species or residual soil P level used in this study.

III. FERTILIZER PLACEMENT WITH REDUCED TILLAGE

Due to concern over erosion control and fuel costs, there is currently much interest in crop production systems requiring less mechanical seedbed preparation than the common methods involving plowing, disking, and spike-tooth harrowing to prepare a smooth, clean seedbed. Several reduced tillage techniques have been developed, but two have become very popular: chisel plowing and no-till planting. Chisel plowing reduces the amount of field surface area inverted during primary tillage; no-tilling results in a soil disturbance of only 2.5- to 7.5-cm width for each planted row and for all practical purposes represents use of no primary tillage. Because of less soil disturbance involved with either no-till or chisel plowing, there has been much interest in how vertical fertilizer distribution affects

root zone fertility levels, particularly with respect to fertilizer application methods necessary to obtain best crop production.

Several authors, including Wells (1984), discuss the effect that continuous no-tillage has on soil properties. Phillips et al. (1980) defines the no-tillage system as:

> *one in which the crop is planted either entirely without tillage or with just* sufficient tillage to allow placement and coverage of the seed with soil to allow it to germinate and emerge. Usually no further cultivation is done before harvesting. Weeds and other competing vegetation are controlled by chemical herbicides. Soil amendments, such as lime and fertilizer are applied to the soil surface.

Review of several papers (Triplett & Van Doren, 1969; Moschler et al., 1973; Bandel et al., 1975; Blevins et al., 1977; Blevins et al., 1978; Doran, 1980; Phillips et al., 1980; Blevins et al., 1980, Randall, 1980; Moncrief & Schulte, 1982; Ketcheson, 1980; Lal, 1979) shows the following effects of no-tillage on soil properties:

1. Soil moisture content. Because of less surface evaporation and better infiltration of rainfall, there is usually 15 to 25% more available soil water during the growing season with no-tillage compared with conventional tillage.
2. Soil temperature. Due to the insulation effect from the surface mulch of killed sod, killed small grain, or previous crop residues, soil temperature changes more slowly under no-till conditions. This results in cooler soil temperatures during the growing season and much less diurnal fluctuation.
3. Organic matter. *In continuous no-till systems, organic residues* from the previous crop collect on the soil surface with subsequent redistribution of soil organic matter compared with conventional tillage. Greater root growth activity *in the top 5 cm of soil resulting* from no-tillage also adds to increased organic matter content in the uppermost part of the soil profile. As a result, organic matter content becomes concentrated at the soil surface with continuous no-tillage, whereas it is mixed somewhat uniformly to plow depth in conventional tillage.
4. Microbial activity. As would be expected from more moisture and accumulation of a concentrated layer of organic residues at the soil surface, there is greater surface microbial activity in no-tilled soils compared with conventionally tilled soils. Greater numbers of both aerobic and anaerobic bacteria have been measured under no-tillage *compared with conventional tillage. Even though large num*bers of aerobes are present, the relatively large presence of anaerobes, together with a high concentration of organic materials and a *higher soil moisture content, results in less potential for oxidation* in no-tilled soils compared with conventionally tilled soils.
5. Residual soil N. Residual soil N content increases in continuous no-till production despite the increased potential for both leaching and denitrification of NO_3^-. It appears, based on the few studies reported, that this increased residual soil N results from the increased concentration of organic residues near the soil surface and that it is in organic form. Indications are that mineralization of this labile pool of organic N *is sufficiently slower in no-tillage* that an increased residual N content develops, even though it is only slowly available to crops in any one year. Because of this, NO_3^- soil tests are *not likely to indicate* the presence of this labile pool of organic N.
6. Bulk density. Some studies have shown little difference in long-term effect of no-tillage on bulk density, indicating that even though annual seedbed tillage in conventional systems initially lowers the plow layer bulk density relative to no-till, subsequent recompaction of the plow layer through the growing season and overwinter results in bulk densities of near the same value as those measured in no-till. Other studies, notably those from the northern Corn Belt have indicated that unless the *plow layer receives some* manner of primary tillage, bulk density is high enough to create problems with some nutrients, particularly K. Because of this, it has been suggested *that fields should test high* in exchangeable K^+ or starter fertilizer containing K should be used for no-tilling in the northern Corn Belt.
7. *Soil pH. Studies indicate* that after 3 to 4 yr of continuous no-till production of corn, a very acid layer 1 to 5 cm thick develops at the surface of the mineral soil. This accelerated acidification related to *no-till has been explained* as resulting from decomposition of the concentrated layer of organic residues on the surface with subsequent intensive leaching by the resultant organic acids in a thin layer at the top of the soil profile. As with conventional tillage systems, this acidification process is increased by use of acid-forming fertilizer N.

It should be emphasized that the effects listed above are largely based on continuous, long-term use of no-till techniques. From the practical standpoint of developing crop production *systems to utilize no-till* techniques, particularly those involving rotations, it is debatable as to whether producers will use no-till continuously in the same field. Most studies reporting on such *long-term effects have lasted 5 to 10* yr due to the relatively recent advent of no-till production systems. Although these studies provide the best current knowledge of no-till effects on soil properties, one *should keep in mind that 5 to 10* yr is probably not long enough to evaluate long-term effects and at best likely represents only directions of change that take place. Care should be taken in interpolating these effects to individual production systems where the field is not continuously no-tilled for long periods of time.

A. Tillage Effects on Mineralization, Incorporation, and Nutrient Stratification

Randall (1980) reported results of 10 yr of field experiments conducted to study some of the fertility problems *involved in shifting* from

are convenient to use in conjunction with irrigation, and lend themselves readily to custom mixing and application. Studies have shown that most fluids are not different in effectiveness from water-soluble solids. Use of suspensions has been growing rapidly in many areas to obtain higher analysis and greater economy than with liquid (solution) fertilizers. The performance of suspensions is equal to that of clear solution materials or dry water-soluble fertilizer materials. Any differences that have been observed can be traced back to either differences in chemical composition or to differences in placement in the soil.

5. *Miscellaneous Phosphates*

TVA has investigated phosphate materials of ultra-high analysis in recent years, but none of these is available commercially. In addition, they have introduced the urea–ammonium orthophosphates and urea–ammonium polyphosphates currently being evaluated in agronomic applications. These materials comprise homogeneous formulations with higher N content, and typical grades would be 28–12–0 (28–28–0) or 35–7.4–0 (35–17–0). Another class of experimental materials are the urea phosphates, 17–19–0 (17–44–0) and materials formulated from urea and urea phosphates. The urea phosphate materials hold promise in dealing with the volatilization loss of ammonia from urea in surface nonincorporated applications, especially in reduced tillage or no-tillage systems. These products could become increasingly important fertilizer sources in the future, particularly in light of the need to improve the efficiency of N utilization.

Among other P sources that have been used as fertilizer are dicalcium phosphate, metaphosphates, basic slag, various calcined phosphates, and unreacted phosphate rock. All of these materials are relatively insoluble in water and range in citrate solubility from slightly to completely soluble. In general they are less profitable than the more soluble phosphates for use in modern intensive agriculture and are used primarily in areas where an abundance of one of the products favors it economically. They are sometimes useful as basic broadcast applications for building up a reserve supply of P in the soil and should be supplemented with small amounts of soluble P for best results in many crops, especially on soils that are not high testing in P.

VIII. PHOSPHORUS FERTILIZATION PRACTICES

Fertilization practices should consist of providing adequate plant available P in the soil throughout the crop growing season. In actual practice, P fertilization must necessarily be adjusted considering the source of P fertilizer, source and quantity of other fertilizer nutrients, the crop and its needs, the yield goal, tillage method and time, fertilizer application method, and other factors that may affect the economics of fertilizer choice and rate.

A. Phosphorus Needs

Determining the need for P is the first step in the fertilization program. The most common method of determining soil P levels is through soil testing by means of chemical extracting agents. The most common extractants include the Bray no. 1 (0.025 *M* HCl + 0.03 *M* NH_4F), the Olsen (0.5 *M* $NaHCO_3$), and the Mehlich or double acid (0.05 *M* HCl + 0.025 *M* H_2SO_4). Such extractants are widely used, and many of them provide an excellent index of P levels in soils, particularly when used in areas of somewhat similar soils for which they are calibrated, as discussed in an earlier chapter.

Interpretation of soil test results to give recommendations on quantities of fertilizer P needed presents a more difficult problem than the actual soil test. Satisfactory interpretation is dependent on correlating soil test levels adequately with actual crop responses in the field to applied fertilizer. Historically, much soil test correlation research has been done in many locations, but more is needed to update fertilizer recommendations based on changes in tillage and techniques of fertilizer application.

The concentration of P determined by the soil test is often interpreted into categories such as low, medium, and high. For most crop and soil conditions, response to fertilizer P will nearly always be obtained on low-testing soils. For soils testing medium, crop response to fertilizer is likely but less frequent; and for soils testing high, crop response is generally infrequent. Therefore, for a soil testing low, recommendation for P normally consists of an amount necessary for optimum economic return from the current year's crop, as determined by field correlation data. Such a rate of P usually results in sustained increase in the soil test level with time. For soils testing in the high range, the most economical rate of P may be that which is sufficient to maintain the present soil test level for most crop and soil conditions. Examples of typical interpretations of soil test P level for three extracting agents are shown in Table 9–2 (Thomas & Peaslee, 1973).

Chemical analysis of plants and plant parts for tissue P concentration is another means of assessing P availability. This method has not been widely used with field crops because of the cost involved and difficulty of interpreting results and the fact that the results are usually obtained too late to permit corrective fertilization of the crop being grown. In recent years, a modified approach to interpreting plant analysis results has been

Table 9–2. Relative categorization of P concentrations into low, medium, and high for three common soil extractants (Thomas & Peaslee, 1973).

	Extractant		
Relative soil level	0.025 *M* H_2SO_4, 0.05 *M* HCl	0.03 *M* NH_4F 0.025 *M* HCl	0.5 *M* $NaHCO_3$
	Extractable P in soil, kg/ha		
Low	0–36	0–34	0–11
Medium	37–83	35–67	12–22
High	84+	68+	23+

developed and is being used in some laboratories and by some researchers. It is known as the DRIS, an acronym that stands for diagnosis and recommendation integrated system (Sumner, 1979). This technique takes into account the interaction among nutrients, which is important to a meaningful interpretation of most plant analysis information. The interpretation requires considerable experience and a wide knowledge of the factors that can affect nutrient levels in plant tissues. Analyses can vary greatly according to the part of the plant sampled, plant age, content of other nutrients, weather conditions, crop variety, and other factors. Researchers are continuing to acquire correlation and other interpretive data that should make this technique more useful in the future.

Field tissue tests, sometimes referred to as *quick tests*, have been used as a field technique for measuring P in the crushed tissue or sap extracted from a part of a growing plant. The use of this technique has been largely in the area of troubleshooting or tentative field diagnosis in problem situations and requires a skilled interpreter for reasonable accuracy and success. It is best used as a preliminary indicator of otherwise obvious plant problems and should be confirmed with a follow-up plant analysis and soil test.

In addition to soil tests and plant analysis, another criterion that can be used to estimate P fertilizer needs is the consideration of the level of P in the subsoil. It may vary widely among soils in any given area and can have a definite influence on whether or not crops respond to P fertilizer. It is thought that particularly during dry periods when the surface soil may be too dry for active root absorption of available P, soils with a high subsoil P level may be better able to supply P to the crop. Numerous states adjust their fertilizer recommendations based on subsoil P levels for given geographic areas and may also adjust those recommendations for variations in soil texture, drainage, pH, and other characteristics.

B. Rates of Phosphorus Fertilization

Phosphorus fertilizer rates vary considerably depending on crop and soil factors previously discussed as well as differences in fertilization recommendation philosophies. In general, the fertilizer recommended at high soil test levels is regarded as an insurance measure with the intention that the recommender wishes to be sure that fertilizer does not become a limiting factor and that crop production is at an optimum level when the soil is testing high.

For low-testing soils there is disagreement regarding buildup of P soil test levels for maximum production. The amount that it takes to build different soils into higher test level ranges varies. Peck et al. (1971) reported field application of 4 mg/kg of P was required to change the Bray no. 1 extractable P by 1 mg/kg in Illinois soils. In Kentucky soils, Thomas and Peaslee (1973) reported it took 3 to 6 mg/kg of P to change the soil test level 1 mg/kg according to the Bray extractant. Griffin and Hanna (1967) reported for New Jersey soils it took 2 to 4 mg/kg of P to change extractable P soil test by 1 mg/kg. In a Virginia soil, 6 to 10 mg/kg of P were required to increase extractable P by 1 mg/kg with the H_2SO_4–HCl extractant (Thomas & Peaslee, 1973), and Rouse (1968) reported an average ratio of about 7:1 for the same extractant on Alabama soils. It is generally regarded that these types of ratios should decrease as the initial level of P increases. Soils having low extractable P require much more added P to increase them to a high level than it does to increase a high-testing soil to a very high-testing one. The economics of soil test buildup have not been shown.

Table 9–3. Approximate nutrient removal of P per harvested crop unit (Colliver, 1981).

Crop	P removal, g/kg
Corn, grain	6.79
Sorghum, grain [*Sorghum bicolor* (L.) Moench.]	7.14
Soybeans, grain	13.3
Wheat, grain	10.0
Wheat, grain + straw [*Agropyron cristatum* (L.) Gaertn.]	13.3
Oats, grain (*Avena sativa* L.)	8.0
Oats, grain + straw [*Arrhenatherum elatius* (L.) Beauv. ex J.&C. Presl.]	12.8
Barley, grain (*Hordeum vulgare* L.)	6.83
Alfalfa and alfalfa-grass, hay (*Medicago sativa* L.)	6.01
Red clover, hay (*Trifolium pratense* L.)	5.01
Bromegrass or tall fescue, hay (*Bromus inermis* Leyss.)	7.01
Bermudagrass, hay [*Cynodon dactylon* (L.) Pers.]	7.01
Corn, silage	1.35
Sorghum, silage [*S. bicolor* (L.) Moench + *S. sudanese* (Piper) Stapf]	1.60
Cotton (*Gossypium hirsutum* L.)	25.4
Peanuts (*Arachis hypogea* L.)	5.51
Sugarbeets (*Beta vulgaris* L.)	0.25
Potatoes (*Solanum tuberosum* L.)	1.60

Researchers recommend basing P fertilizer rate on the soil test and other soil factors and maintaining fertilization according to crop removal. See Table 9–3 for estimated amounts of P removal by selected field crops.

C. Time and Method of Application

In theory, P fertilizer should not be applied very far in advance of seeding the crop, because soluble phosphates tend to revert to less available forms in the soil with time. In actual practice, however, the timing of P fertilizer application is dependent on the availability of labor, equipment, and time to do the job within the overall cultural practices for the particular crop to be grown.

Placement of fertilizer P in soil in a position and form that will be readily available to the growing plant is likely much more important than the actual timing of fertilizer application. Because of the limited movement of P in the soil, fertilizer P should initially be placed in the proper position with respect to the plant root system and soil moisture supply.

Uniform broadcast application of fertilizer P is feasible in either dry or fluid form. Subsequent incorporation of the broadcast fertilizer by tillage mixes it into the soil and places a part of the P deep enough in the soil for it to be in a moist zone during at least some portion of the growing season.

With soils containing low levels of available P, the time and method of application may be quite important. Placement in the effective rooting

zone (and relatively close to the time of actual crop need) generally results in greater efficiency of P utilization. However, on soils containing medium to high levels of available P, the time and method of application assume less importance. In a rotation experiment in Indiana (Barber, 1969), broadcast P fertilizer was applied once every 4 yr at rates of 98 and 196 kg/ha of P over a 16-yr period. Both rates were effective in maintaining yields through the fourth year following each application. Barber concluded that more flexibility in P application is possible without seriously affecting yield provided that the P is plowed under or mixed deeply into the soil.

It is generally accepted that the efficiency of banded fertilizer application is at least equal to and often greater than that for broadcast application. However, this potential agronomic-economic advantage for banding has been ignored by many growers because most banding is considered an "at planting" operation. The inconvenience of banding fertilizer during

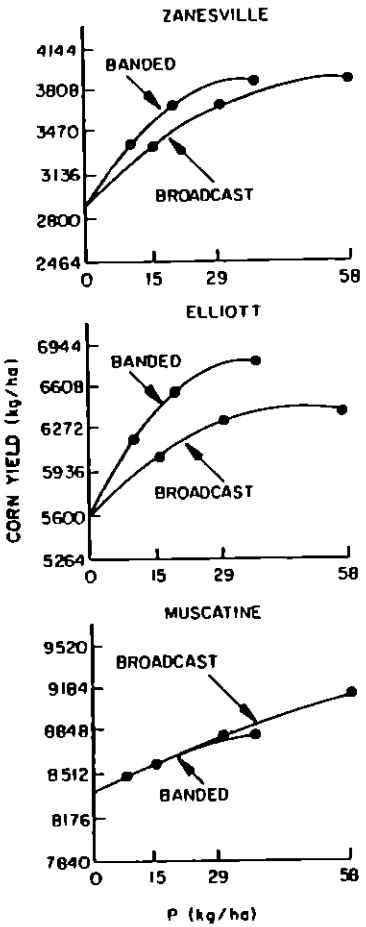

Fig. 9–12. Corn yields on three Illinois soils vs. banded and broadcast rates of P (Welch et al., 1966).

the planting operation has resulted in the preference for broadcasting, especially due to the ease and cost efficiency of custom application. However, with continued increases in crop production cost, many growers now are more receptive to banding to improve fertilizer use efficiency.

Generally, the closer to the time of plant utilization that the nutrient is applied, the greater the efficiency of uptake. Therefore, band application may give greater efficiency because there is less immobilization of P by either microbial, chemical, or physical means.

Work by Welch et al. (1966) in Illinois is shown in Fig. 9–12 in which banded and broadcast P are compared on three soils with corn. The Zanesville (fine-silty, mixed, mesic Typic Fragiudalfs) and Elliott (fine, illitic, mesic Aquic Argiudolls) soils have greater efficiency of P use when banded. In the Muscatine (fine-silty, mixed, mesic Aquic Hapludolls) soil the methods gave equal results. Table 9–4 shows the properties of these three soils, and even though the subsoil P levels were not clearly defined, it is known that Muscatine has higher subsoil P levels than the other two soils. The percentage yield increase due to P was greatest with the Zanesville (very low surface and subsoil P), followed by the Elliott (somewhat better P status), and then by the Muscatine, which would have the best P status of the three considering both top and subsoil. Therefore, the relative efficiency of the two application methods seems to be related to the P fertility status of the soil.

In Table 9–5, Welch et al. (1966) show the amounts of broadcast P required to produce the same corn yield as given rates of banded P. For example, with 20 kg/ha of P banded, the broadcast rate required to give equal yield was 30 kg/ha of P. The calculations show a range of efficiency of 0.49 to 0.88 for the Zanesville and Elliott soils, but the relative efficiency for the Muscatine was generally 1.0 or slightly greater.

As indicated above, band applications of P are frequently applied for

Table 9–4. Properties of three soils differing in response to P fertilization (Welch et al., 1966).

	Zanesville	Elliott	Muscatine
pH	5.8	6.0	6.5
Bray P-1, kg/ha	6	20	18
Subsoil P	--	--	Higher
Percent yield increase of P	51	30	12

Table 9–5. Band vs. broadcast P for equal corn yield and relative efficiency on three soils (Welch et al., 1966).

	Broadcast P					
Banded P	Zanesville		Elliott		Muscatine	
kg/ha	kg/ha	Eff.	kg/ha	Eff.	kg/ha	Eff.
10	15	0.64	20	0.49	10	0.99
20	30	0.65	--	--	19	1.05
29	43	0.70	--	--	26	1.12
39	45	0.88	--	--	32	1.23

Table 9–6. Corn yields vs. P and starter in northwest Iowa on Primghar sl (fine-silty, mixed, mesic Aquic Hapludolls) with a corn-oats-meadow rotation (Webb, 1977).

Plowed down every 3 yr	Starter†	Corn yield	
		1977	1957–1977
kg/ha		metric tons ha^{-1}	
0	–	5.77	5.39
	+	6.59 (+0.82)	6.21 (+0.82)
22	–	7.28	6.62
	+	7.53 (+0.25)	6.77 (+0.26)
45	–	7.28	6.84
	+	8.03 (+0.75)	7.02 (+0.18)
67	–	7.90	6.84
	+	8.03 (+0.13)	6.90 (+0.06)

† Starter = 129 kg/ha as 5–8.7–8.3 (5–20–10).

increased efficiency of utilization compared with broadcast methods. Row applications of P are frequently applied primarily for early season or starter effects and may be applied over and above those amounts in broadcast applications. Band applications may be a satisfactory means of applying all of the needed P (on soils with relatively high levels of available P). Drilling of the fertilizer with the seed is a very effective means of fertilizing small grains and other crops seeded in close row spacings.

A long-term study from northwest Iowa shows effects of banded starter fertilizer on corn yields (Webb, 1977; Table 9–6). The study is a rotation of corn-oats-meadow and the rates of P are plowed down every 3 yr. Superimposed on the P treatments are either no starter, or a banded starter of 129 kg/ha of 5–8.7–8.3 (5–20–10). The numbers in parentheses are the corn yield increases due to the starter fertilizer. The response to starter over 21 yr is positive, but it is less where the higher P rates have built up soil test P levels.

A second long-term study reported on by Webb and Angstrom (1978) in Table 9–7 is from north central Iowa. The results are very similar to

Table 9–7. Corn yields vs. P and starter in north central Iowa on Webster sicl (fine-loamy, mixed, mesic Typic Haplaquolls) with a corn-oat-meadow rotation (Webb & Angstrom, 1978).

Plowed down every 3 yr	Starter†	Corn yield	
		1978	1957–1978
kg/ha		metric tons/ha	
0	–	6.59	5.39
	+	7.78 (+1.19)	6.65 (+1.26)
22	–	8.03	7.34
	+	9.72 (+1.69)	7.97 (+0.63)
45	–	8.78	7.65
	+	9.78 (+1.00)	8.03 (+0.38)
67	–	9.03	7.71
	+	8.91 (−0.12)	8.15 (+0.44)

† Starter = 129 kg/ha as 5–8.7–16.7 (5–20–20).

those just discussed for Table 9–6. The main difference is that the average response to banded starter of 129 kg/ha of 5–8.7–16.7 (5–20–20) is even greater over the 2 yr of the study than in the previously discussed example. Even at the highest rate of plowed down P, there is still an average of 0.44 metric tons/ha increase due to starter. Those two studies do not directly compare band to broadcast fertilizer, but they do show that even with adequate broadcast P, there is an additional advantage to adding some banded starter fertilizer under conditions of those studies. Similar results have been reported in other more northern corn-growing areas and are sometimes in contrast to the more southern, warmer locations where starter response is less likely to occur.

For wheat in Nebraska, low soil P levels may require three times as much broadcast P to achieve the same yield as with an appropriate amount of banded (Peterson et al., 1981). At medium to high soil levels, P requirement is the same for both placement methods.

Barber (1974) proposed a method of fertilizer placement that is somewhat of a compromise between banding and broadcasting. He called it *strip placement*, accomplished by banding 5-cm wide strips of fertilizer on the soil surface in 71-cm spacings and then moldboard plowing. During plowing there is limited mixing of fertilizer with the soil, leading to wider distribution than in normal banding but less than in broadcast. This concept is diagrammed in Fig. 9–13. The theory is that strip placement would allow better root exploration of the fertilizer than in ordinary banding, and at the same time minimize soil reaction with fertilizer that may be prevalent in broadcasting where soil-fertilizer contact is greater. Table 9–8 shows 5-yr average corn yields comparing the three placement methods and shows the strip placement having an advantage. This response to strip placement occurred on a soil testing low in available P. Subsequent experiments on higher testing P soils did not show the same advantage. The conclusion is that the potential advantage of strip application is greatest on soils testing low in P.

Another approach to banding fertilizer for improved efficiency is the dual application of N and P materials by injection into soil as described by Murphy et al. (1978). In P-responsive soils, they found agronomic superiority in winter wheat for P dual knifed with N compared with either

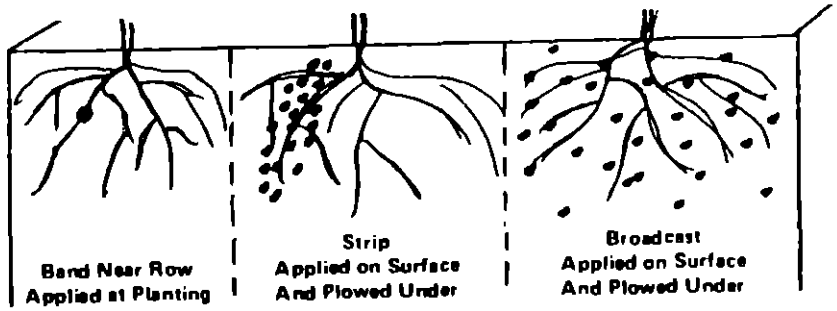

Fig. 9–13. Schematic presentation of distribution of P in soil when applied by three different methods (Barber, 1974).

Table 9-8. Effect of P fertilizer placement on yield of corn and P concentration of the ear leaf at tasseling (Barber, 1974).

Treatment	Yield	Leaf P conc	P soil test†
	metric tons/ha	%	kg/ha
Band by row	7.21	0.26	14
Broadcast and plowed under	7.69	0.27	21
Strip and plowed under	8.28	0.29	37
LSD (0.05)	0.36	0.02	9

† Soil sampled between rows at random during fifth year and tested by Bray P-1 procedure.

broadcast or drill applications. Materials used were either anhydrous ammonia or urea–ammonium nitrate solution and liquid ammonium polyphosphate as fluid materials and solid N-P materials. The positive effect is attributed to deep placement of the N + P nutrients regardless of their form.

Data reported by Leikam et al. (1978) in Table 9–9 show that when N either as anhydrous ammonia or urea-ammonium nitrate solution is dual knifed with ammonium polyphosphate solution, higher grain yields of wheat are achieved as well as higher leaf concentrations of P when compared with methods of N and P application where most of the two nutrients were applied separately. Deep placement of N + P again is the primary reason for the better results.

The interpretation of the apparent advantage of dual placement centers on two most likely effects. Deep placement of N and P for dryland crops in the Great Plains can involve greater nutrient availability due to the fertilizer being placed in soil moisture at lower soil depths. Also, the enhancement of P uptake by the presence of ammonium ions in the soil has been identified as a factor in P absorption for many years. Olson and Drier (1956) reported that NH_4^+-N enhanced P absorption in Nebraska. Riley and Barber (1971) reported that ammonium N influences P absorption in a positive way through a decrease in soil pH in the vicinity of plant roots as the plant absorbs ammonium ions.

Tillage implements and ammonia applicators can be equipped for dual applications of ammonia and fluid fertilizers (Follett et al., 1981; Fig. 9–14). The ammonia and liquid lines must be kept separate to prevent vaporizing ammonia from freezing the fluid line. Separation by 2 or 3 cm at the delivery points of both lines prevents freezing. Vertical separation of the release points (2–3 cm) on shank-type applicators prevents accumulation of solid ammonium polyphosphate compounds around the holes in the fluid line. These result from reactions of the ammonia and liquid ammonium polyphosphate.

In addition to the dual application of ammonia and fluid fertilizer, there is also equipment available for the delivery of dry fertilizer in dual application. Pneumatic systems for the delivery of dry fertilizer through tubes allows the simultaneous application of dry products down the back of the same shank in which ammonia is applied. Dual application of N and P materials, particularly when combined with a tillage operation, provides

Table 9-9. Comparative effectiveness of methods of N-P application on grain yield and leaf concentrations for wheat in Kansas (Leikam et al., 1978).

	Reno County			Ellsworth County			Labette County	Dickinson County	
Method†	metric tons/ha	% N	% P	metric tons/ha	% N	% P	metric tons/ha	% N	% P
No N	1.4	3.80	0.17	2.6	3.91	0.20	1.7	3.58	0.22
Knifed ammonia	1.5	3.44	0.16	2.9	3.90	0.16	2.6	4.14	0.23
Knifed ammonia, knifed APP	2.6	3.74	0.25	3.9	4.74	0.30	3.0	4.50	0.28
Knifed ammonia, broadcast APP	2.6	3.78	0.20	3.6	3.92	0.19	2.9	4.06	0.22
Knifed ammonia, band APP	2.4	3.80	0.19	3.4	4.18	0.21	2.8	4.12	0.24
Knifed UAN	1.7	3.84	0.16	2.7	4.02	0.19	2.5	4.07	0.23
Knifed UAN, knifed APP	2.9	3.87	0.23	3.7	4.62	0.29	3.0	4.02	0.28
Knifed UAN, broadcast APP	2.6	3.82	0.20	3.5	4.02	0.20	3.0	3.92	0.21
Knifed UAN, band APP	2.4	3.84	0.20	3.0	4.06	0.21	3.0	4.07	0.23
Knifed ammonia, knifed APP	2.6	3.74	0.25	3.9	4.74	0.30	3.0	4.50	0.28
Knifed ammonia, knifed APP plus N-SERVE	3.2	4.02	0.23	3.0	4.49	0.30	3.3	4.36	0.33
Soil pH		7.3			6.0		5.5	6.1	
Soil test P, kg/ha		9			11		9	26	

† APP is ammonium polyphosphate supplied as 11-16.2-0 (11-37-0) from TVA at rate of 19 kg/ha P (N constant at 84 kg/ha N). UAN is nonpressure, 28% urea-ammonium nitrate solution. N-SERVE is a nitrification inhibitor product of Dow Chemical Company (Midland, MI). Band means placement of P with seed.

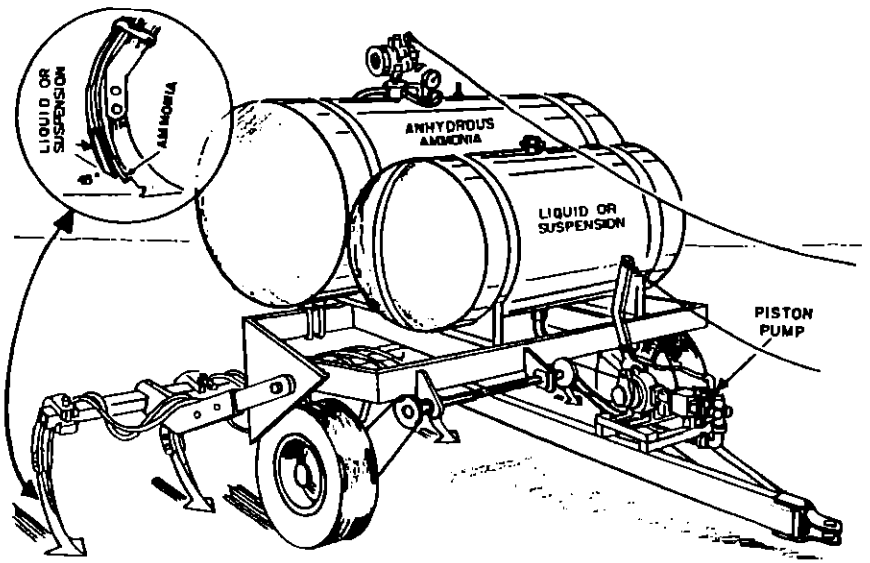

Fig. 9-14. Applicator for the dual-knife application of anhydrous ammonia and fluid fertilizers (courtesy of TVA, [Anon., 1982, p. 72]).

both agronomic and economic advantages to the grower. The trend towards fewer trips across the field by growers will likely result in increasing use of this method of fertilizer application.

In some areas, P application is accomplished by injecting either orthophosphoric acid or ammonium polyphosphate solution into irrigation water. As long as precipitation of P compounds is avoided, distribution of P should be satisfactory. However, P still should be applied early in the growing cycle before seeding and, for most cropping situations, it should be incorporated in the plant root zone. Follett et al. (1981) point out that problems in application of P in irrigation water are at least threefold:

1. Precipitation may be encountered when ammonium polyphosphate-containing liquids are injected into high Ca or Mg water.
2. Phosphorus must be applied very early in the growing cycle for most crops, particularly if there is a definite P need to prevent any early season suppression of yield potentials.
3. Phosphorus applied for row crops through irrigation water may remain on or near the soil surface if not incorporated and be less effective than P applied preplant and incorporated by a tillage operation. The latter problem, however, may be insignificant in the irrigation of crops such as alfalfa and grasses.

D. Cropping and Tillage Systems

In recent years there has been considerable attention given to the P fertilization of crops grown in systems of reduced tillage or no-tillage. Reduced tillage systems are used to reduce soil erosion, conserve water, and to decrease production costs. They may vary from elimination of a single conventional tillage operation to almost complete elimination of tillage except for planting. Such systems offer less opportunity for incorporation of P fertilizers to any appreciable depth in soil. Suggested methods of fertilizer application have included row placement supplemented by the occasional plowing under of a heavy rate of P, band placement with knives or other devices, and surface placement with whatever mixing is provided by tillage operations. Phillips and Young (1973) stated that no-tillage results in keeping the upper part of the soil profile sufficiently moist to ensure P availability for plants. They suggest that incorporation of fertilizer below the soil surface is not necessary. They also suggest that in no-tillage there is proliferation of active roots in the very shallow soil surface that results in sufficient uptake of P so that incorporating to deeper depth is not necessary. However, climate variability and droughty spells may limit surface moisture during critical nutrient uptake periods even if there are large amounts of crop residue on the surface. Subsurface placement of P fertilizer provides a hedge against such eventualities.

From an environmental standpoint, runoff and erosion of surface soils containing large amounts of unincorporated P fertilizer can be a detrimental source of surface water pollution. Randall (1980) recognized the problem of positional unavailability of P that can occur especially in dry years when root activity in the soil surface layer is decreased in the area of major concentration of available P. His results in Minnesota are shown in Table 9-10 with the reduced tillage treatments. Much of the added P along with the P brought up by the roots and recycled into the crop residue was concentrated in the top 0.102 m of the soil profile. With moldboard plowing, P was distributed evenly throughout the top 0.305 m of soil. Continuous chisel plowing resulted in P being incorporated to a depth of 0.152 m after 8 yr but to a depth of only 0.102 m after 4 yr. Randall recommended a preventive measure to minimize low P fertility: Soil P should be built up to high levels throughout the soil plow layer before switching to reduced or conservation tillage systems. He further suggested that a farmer's tillage

Table 9-10. Influence of continuous tillage methods on the distribution of soil P within the 0- to 0.305-m profile at Waseca, MN after 4 yr (1973) and 8 yr (1977) (Randall, 1980).

	Primary tillage			
Depth	Moldboard plow	Chisel plow	Disk	No tillage
m	P, soil test, kg/ha			
	1973			
0-0.051	76	110	121	121
0.051-0.102	76	81	63	54
0.102-0.152	74	43	34	36
0.152-0.229	54	20	18	27
0.229-0.305	27	9	9	9
	1977			
0-0.051	63	128	152	155
0.051-0.102	65	116	119	96
0.102-0.152	72	85	56	49
0.152-0.229	78	40	31	38
0.229-0.305	49	20	18	27

system should include moldboard plowing occasionally in a reduced tillage system to redistribute soil P throughout the profile. This could be done perhaps once every 4 or 5 yr for adequate redistribution of P.

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10

Production, Marketing, and Use of Potassium Fertilizers

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The production, marketing, and use of potassium fertilizers is very important for crop production. This is especially true in the more humid regions where soils are more often deficient in K. Significant changes have occurred in recent years in production methods, materials produced, marketing procedures, and methods of application of K. This chapter discusses these changes.

1. POTASSIUM FERTILIZER PRODUCTION

Commercial scale production of K fertilizers began in Germany about 1861, approximately 15 yr after Liebig found that K is an essential element for plant growth. German salt deposits were being mined at the time for the production of common salt. Potassium salts, present in some of the run of mine ore, were regarded as contaminants and rejected from the salt production operations as wastes. Thus, when needed for fertilizer K production, the mines were in place. What remained to be accomplished was the construction of refining facilities to upgrade the crude K-containing salts into agriculturally useful products. This challenge was met by German chemists, resulting in the birth of the modern K fertilizer industry. Due to a favorable reserve position and technical expertise, Germany was essentially the only source of agricultural-grade K salts until World War I. This situation began to change at that time when France acquired the Alsatian

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12

Production, Marketing, and Use of Calcium, Magnesium, and Micronutrient Fertilizers

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Increased knowledge acquired since 1960 about plant requirements as well as sources and effective methods of applying secondary nutrients and micronutrients has resulted in increased use in the USA. Improvements in soil and plant analyses have provided additional knowledge of specific crop needs and also of the wide variations in crop response to secondary nutrients and micronutrients found under field conditions. Higher rates of mixed NPK fertilizers and higher crop yields have increased the need for lime and may have increased the need for micronutrients.

In the first edition of this book, separate chapters covered secondary and micronutrient fertilizer production (Tisdale & Cunningham, 1963) and plant requirements, soil pH effects, and methods of application (Berger & Pratt, 1963). These subjects, except S, which was discussed separately, were consolidated in the second edition (Mortvedt & Cunningham, 1971). Several books on micronutrients (Sauchelli, 1969; Mortvedt et al., 1972; Davis, 1980) have been published; thus, this discussion will not include all of the subject matter covered in depth in the above references.

I. PRODUCTION METHODS

A. Nutrient Sources

Production methods of Ca and Mg fertilizers are not included in this section because dolomitic limestone generally is used to supply these nutrients; supplying Ca and Mg with sources other than limestone is discussed later.

Less than 10% of the industrial production of micronutrient elements in the USA is for agricultural use. For example, about 90% of the Mn im-

ported into the USA is used for steel production. Because of the relatively minor fraction used in agriculture, it is difficult for those in metal industries to understand the seasonal need for fertilizers compared with year-round industrial needs. Therefore, the fertilizer industry is faced with the problem of obtaining sufficient micronutrient sources to meet demands each spring. Storage due to stockpiling increases costs.

1. Inorganic Sources

Inorganic sources include naturally occurring ores, manufactured oxides, carbonates, and metallic salts such as sulfates, chlorides, and nitrates. Some oxides, such as cuprous oxide (Cu_2O), may be used as mined, but plant availability of other oxides, such as naturally occurring manganese dioxide (MnO_2), is so low their use is not recommended. Inorganic sources usually are the least expensive per unit of micronutrient, but they are not always the most effective for soil application.

Sulfates are by far the most common of the metallic salts, and their physical properties make them suitable for use with mixed fertilizers. Although these sources also add plant-available S to soils, the amount of S applied at most recommended micronutrient rates is low. Ground ores or oxides are treated with sulfuric acid (H_2SO_4) to produce crystalline sulfate materials. Some of these products can be made in granular form by extrusion, compaction, or granulation by several methods. Oxysulfates, especially of Zn and Mn, are produced by partial acidulation of oxides.

Metal-ammonia complexes also are used as micronutrient sources. Ammoniated zinc sulfate ($ZnSO_4$) solutions are marketed widely and are compatible with most fluid fertilizers. The most common product contains 10% N, 10% Zn, and 5% S.

Borax ores found in old geological lake deposits are mined, milled, and refined to remove impurities. The most common source of ores was $Na_2B_4O_7 \cdot 10H_2O$, but products containing fewer waters of hydration now are used more widely. Granular borates are produced for use with bulk-blended fertilizers. Finely ground borates are produced for foliar sprays and for incorporation with fluid fertilizers.

Molybdenum sources are produced from molybdenite (MoS_2), which is mined in Colorado, and from by-products of Cu mining in Utah (Hurlbert, 1952). Both sodium molybdate (Na_2MoO_4) and ammonium molybdate [$(NH_4)_2MoO_4$], the main fertilizer sources of Mo, are produced by ore purification, roasting to form oxides, and through subsequent solubilization reactions.

Zinc sources are produced by several processes. Metallic Zn (dross) is milled and roasted to form zinc oxide (ZnO). The French process produces fine particles of pure ZnO that are used as a paint pigment, but the material is too expensive for fertilizer use. Sphalerite (ZnS) also is roasted to form ZnO. Zinc sulfate ($ZnSO_4 \cdot H_2O$) is produced by reacting ZnO with H_2SO_4. Partially acidified products also are sold; amounts of water-soluble Zn are directly related to the proportion of $ZnSO_4$ present in those products.

2. Organic Sources

Organic sources include synthetic or natural chelates, natural organic complexes, and combinations of the above. Effectiveness of these sources for plant utilization varies widely. Synthetic chelates generally are more expensive than other sources but may be more effective under certain soil conditions.

Chelates are formed by combining a chelating agent with a metal through coordinate bonds. Chelates may be synthetic (manufactured) or natural (from sugars or from natural products). A chelating agent is a compound containing donor atoms that can combine with a single metal ion to form a cyclic structure called a *chelation complex* or, more simply, a *chelate*. The descriptive word "chelate," derived from the Greek "chela" or "claw," was proposed for this kind of molecular structure in 1920 (McCrary & Howard, 1979). The stability of the metal-chelate bond generally determines plant availability of the applied nutrient. An effective chelate is one in which the rate of substitution of the chelated micronutrient for cations already in the soil is low, thus maintaining the applied nutrient in chelate form for sufficient time to be absorbed by plant roots.

Some chelating agents used for production of micronutrient chelates are:

1. Ethylenediaminetetraacetic acid (EDTA)
2. *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA)
3. Diethylenetriaminepentaacetic acid (DTPA)
4. Ethylenediamine di(*o*-hydroxyphenylacetic acid) (EDDHA)
5. Nitrilotriacetic acid (NTA)
6. Glucoheptonic acid
7. Citric acid

The most common chelating agent used as a micronutrient source is EDTA. There are seven commonly known synthesis routes to EDTA, but four processes are commercially used (Strauss et al., 1983). Two methods are two-step processes involving production of a cyanomethyl derivative of formaldehyde and subsequent saponification by sodium hydroxide (NaOH). The other methods go directly from ethylenediamine to the final product in a single step, using sodium cyanide (NaCN) or hydrogen cyanide (HCN). Metal chelates generally are produced by reaction of the Na chelate salt with a metal; metal chlorides are preferred because metal sulfates result in precipitation of sodium sulfate (Na_2SO_4). Another process increases the pH of the chelate to between 4 and 5 with sodium hydroxide (NaOH), potassium hydroxide (KOH), or ammonium hydroxide (NH_4OH). Metal oxides, which are less costly than the chlorides, may be dissolved in this chelate. After complete solubilization, more caustic is added to bring the pH to between 7 and 8. The caustic source determines the amount of metal that can be carried in the final solution. For example, the highest concentration of Zn in EDTA solutions is 6.5 to 7.0% with NaOH, 8.0 to 9.0% with KOH, or 9.0 to 9.5% with NH_4OH.

Many chelates are sold in liquid form in the USA because production costs per unit of micronutrient are lower than those of the powder form, which requires drying. Liquid chelates are sold mainly for mixing with fluid fertilizers. Dry chelates are incorporated in some granular fertilizers, but their use is generally restricted to specialty products for lawns and gardens.

Natural organic complexes are made by reacting metallic salts with organic by-products of the wood pulp industry. Several classes of these complexes are the lignosulfonates, phenols, and polyflavonoids. The type of chemical bonding of the metals to the organic components in the above products is not well understood. Some of the bonds may be similar to those in chelates, but the remainder are not well defined, hence, the term *complexes*.

Digest liquors from the wood pulp industry contain organic complexes in the Ca or Na form. These liquors are concentrated to about 40% solids, and a micronutrient source is added to form a metal complex. Oxides may be added in this process, but sulfates are preferred because they are soluble. Digest liquors from the Sulfite process contain lignosulfonates that complex metals. Liquors from the Kraft process of pulp production must be sulfonated to improve their complexing capacity, which increases their cost. The most popular complexes are of Zn and Fe, although limited amounts of Cu and Mu complexes are produced. Products containing more than one micronutrient are made for foliar sprays or for application with irrigation water.

3. Fritted Glasses

Fritted micronutrients are glassy products whose solubility is controlled by particle size and change in matrix composition. The powdered raw materials are dried, mixed with silicates or phosphates, and melted in a furnace. This molten matrix then is quenched, dried, and milled. Products may be compacted or granulated prior to bagging and storage. More than one micronutrient may be included to provide custom mixes for various crops.

4. Industrial By-products

Many by-products are being marketed as fertilizers since regulations restrict indiscriminate disposal of industrial wastes. The most common micronutrient industrial by-products contain Mn or Zn. Use of industrial by-products as Zn sources has increased dramatically; flue dusts and baghouse dusts from galvanizing, pigment, rubber, battery, and other industries are used widely. Leaching processes are used to remove many impurities from these products, but some ZnO products are used without purification. Zinc chlorides, nitrates, sulfates and oxysulfates, and manganese sulfate ($MnSO_4$) also are available as industrial byproducts.

Some by-products may also contain appreciable amounts of heavy metals such as Cd, Cr, Ni, and Pb. Plant availability of these heavy metals is not well known, but since their soil application rate is very low, their effects should be minimal. For example, applying ZnO (70% Zn) containing 1000 mg/kg of Pb to soil at a rate of 5 kg of Zn/ha would result in a rate of 0.007 kg of Pb/ha. Because these heavy metals are relatively immobile in soil, they will accumulate in the surface layer and may eventually build up to significant levels if such by-products are applied to a field for a number of years.

B. Incorporation With Mixed Fertilizers

Recommended rates of micronutrients usually are < 10 kg/ha. This makes it difficult to apply micronutrient sources separately and uniformly in the field. Therefore, both granular and fluid NPK fertilizers are used widely as carriers of micronutrients. Including micronutrients in mixed fertilizers is convenient and allows more uniform distribution with conventional application equipment. Costs also are reduced by eliminating the separate application of micronutrients.

Chemical reactions between the micronutrient source and one or more components of the macronutrient fertilizer may occur during manufacture, in storage, or after soil application. Reaction products may differ markedly according to sources, pH of the mixture, and temperature (Lehr et al., 1967). Plant availability of the reaction products may differ from that of the original sources. Therefore, care must be taken to select those micronutrient sources and mixed fertilizers that, when combined, result in products that supply micronutrients in a plant-available form.

Micronutrient sources can be added to mixed fertilizers by incorporation during the manufacture of granular fertilizers, coating granular fertilizers, bulk blending with granular fertilizers, or mixing with fluid fertilizers. Advantages and disadvantages of each method are discussed in the following sections.

1. Incorporation During Manufacture of Granular Fertilizers

Incorporation uniformly distributes micronutrients throughout NPK fertilizers. During manufacture, the micronutrient source is in intimate contact with the mixed fertilizer components under conditions of high temperature and moisture. This enhances the rate of chemical reactions that may decrease the plant availability of some incorporated micronutrient sources. For example, when ZnEDTA (or any synthetic chelate) is mixed with superphosphate before ammoniation, acid decomposition of the chelate molecule results in decreased availability of the applied Zn (Ellis et al., 1965). When the process is changed by adding the ZnEDTA with the ammoniating solution, plant availability of Zn is increased (Brinkerhoff et al., 1966).

Granulation of either $ZnSO_4$ or ZnO with orthophosphate fertilizers having saturated salt solutions of relatively high pH results in Zn products low in initial availability to plants. Yet ZnEDTA remains available to plants when granulated with the same fertilizers (Mortvedt & Giordano,

1969). The reaction products of Zn salts and orthophosphate fertilizers, zinc ammonium phosphate ($ZnNH_4PO_4$), and zinc phosphate tetrahydrate [$Zn_3(PO_4)_2 \cdot 4H_2O$] were available for corn (*Zea mays* L.) when finely divided and mixed with soil but not when applied as granules (Allen & Terman, 1966). Also, ZnO was as effective as $ZnSO_4$ for corn when both sources were applied as fine powders, but only $ZnSO_4$ was effective as a granular material. Distribution of applied Zn in the soil thus may be more important than the water solubility of the Zn sources. Incorporating $ZnSO_4$ with superphosphates before ammoniation results in decreased water solubility of Zn (Jackson et al., 1962). Initial plant availability of applied Zn decreases with level of water-soluble Zn in ammoniated phosphates (Mortvedt, 1968). Other problems encountered with incorporation of micronutrients during manufacture of mixed fertilizers are discussed elsewhere (Achorn & Mortvedt, 1977).

The greatest disadvantage of incorporation during manufacture is that special handling and storage of numerous tons of special fertilizers increase distribution costs. Furthermore, micronutrient concentrations in the fertilizers cannot be changed to meet customer needs. This production method is thus usually limited to fertilizers that can be used on large land areas.

2. *Coating Granular Fertilizers*

As with incorporation during manufacture, coating micronutrients onto granular fertilizers can result in uniform application. The coating procedure consists of dry mixing the granular fertilizers with a finely ground (−100-mesh size) micronutrient source, then spraying a liquid binder and continuing the mixing process. The total cycle takes about 5 min per batch in small rotary mixers and longer periods for larger mixers. Mechanisms of binding action by the liquid are mechanical or by promoting formation of reaction products on the surface of the fertilizer granules (Silverberg et al., 1972).

The coating agent must be inexpensive, must adhere to the fertilizer during handling, and must not cause undesirable physical properties. Water, oils, waxes, ammonium polyphosphate, and urea–ammonium nitrate solutions have been used as binding agents. Water may be used where an increase in granule surface moisture does not promote caking. Oil should not be added to mixtures containing ammonium nitrate (NH_4NO_3) because of the explosion hazard, and not > 1% by weight of oil should be used in other mixtures to prevent oil from seeping through the fertilizer bags. Fertilizer solutions as binding agents are preferred because the fertilizer grade is not decreased appreciably. Some binding materials are unsatisfactory because they do not maintain the micronutrient coatings during bagging, storage, and handling operations, resulting in segregation of finely ground micronutrient sources from fertilizer granules.

The required amount of coating agent ranges from 1 to 3% and varies with the amount and physical state of the micronutrient source and the granular fertilizer. Fertilizer salt solutions and water provide chemical bonds; oils provide mechanical adherence. Fertilizer solution binders may promote caking, whereas some lighter oils penetrate and thereby weaken bags. In the former case, conditioning agents may be added to prevent caking.

Agronomic effectiveness of micronutrients coated onto soluble granular fertilizers should be similar to that with incorporation during manufacture. Ellis et al. (1965) reported that navy bean (*Phaseolus vulgaris* L.) yields were similar with either $ZnSO_4$ or ZnO incorporated during manufacture or coated onto a granular mixed fertilizer, but Zn uptake was higher with $ZnSO_4$ (Table 12–1). They also reported that ZnEDTA remained completely water soluble when coated onto a NPK fertilizer in conjunction with $MnSO_4$, whereas it was only 40% water soluble when coated with MnO onto the same fertilizer. Yields of navy beans also were lower with the latter product.

The nature of the binder does not appear to affect Zn availability to plants. Dissolution of Zn coated onto ammonium polyphosphate or monoammonium phosphate ($NH_4H_2PO_4$) granules as $ZnSO_4$ or ZnEDTA was similar in moist soil whether the coating agent was a fertilizer salt solution or a mixture of diesel oil and soft wax (J. J. Mortvedt and P. M. Giordano, 1966, unpublished data). Use of oil to coat ZnO and MnO onto 8–14–13 (8–32–16) fertilizer granules did not have a significant effect on Zn and Mn uptake by corn and soybeans [*Glycine max* (L.) Merr.] in field experiments (Jones, 1969).

One disadvantage of coating micronutrient sources onto granular fertilizers is higher production costs due to the batch process, which requires more handling. Coating provides more flexibility than incorporation in obtaining the recommended grades for separate fields, but it is not widely used in the USA.

3. *Bulk Blending with Granular Fertilizers*

The main advantage of bulk blending is its flexibility to make small batches of many grades. Thus, micronutrient sources can be blended with mixed fertilizers to produce grades that will provide the recommended micronutrient rate for a given situation. Blending should be done just prior to application, so that there is less chance for chemical reactions to occur that

Table 12-1. Yield and Zn concentration of navy beans as affected by Zn source and method of inclusion with a granular NPK fertilizer (Ellis et al., 1965).

Zn source†	Method of inclusion	Yield	Zn in plants
		kg/ha	mg/kg
--	--	12 320	20
$ZnSO_4$	Blended	16 580	40
$ZnSO_4$	Incorporated	16 360	31
$ZnSO_4$	Coated	16 690	34
ZnO	Incorporated	16 240	23
ZnO	Coated	16 690	26
LSD (0.05)	--	1 680	3

† Fertilizers banded at planting to supply 3 kg of Zn/ha.

would decrease availability to plants. A procedure to put the proper amount of micronutrient in each batch is required, and a longer mixing time to obtain a uniform mix is desirable. Extra bin space is eliminated with the special batches are prepared just before delivery. The popularity of this method of applying micronutrients has increased in recent years but now seems to have reached a plateau. Results of a 1984 survey conducted by TVA and the Association of American Plant Food Control Officials (AAPFCO) showed that there were 5200 bulk-blending plants in the USA with a total annual production of 20 million metric tons of fertilizer (Hargett & Berry, 1985). Micronutrients were being added to bulk blends at 73% of these plants in 1984 compared with 45% in 1974.

The main disadvantage in applying micronutrients with bulk-blended fertilizers is that segregation of nutrients can occur during the blending operation and subsequent handling. Segregation results in nonuniform application of nutrient, which is critical with micronutrients since their application rates are quite low. Studies have shown that the chief cause of segregation is differences in particle size, although particle shape and density also have an effect (Silverberg et al., 1972). Mechanical devices to minimize coning and segregation of materials during handling and storage are available (Achorn & Mortvedt, 1977). A comparison of micronutrient distribution in bags with incorporated ZnO and bulk-blended MnO is shown in Table 12–2. Concentrations of Zn were uniform in all bags, but those of Mn were unacceptably variable. Obviously, fine MnO had segregated from the granular fertilizer during blending and bagging operations.

Incorporation of a micronutrient source with one component of a bulk blend also has been used. This requires a higher micronutrient concentration in the particular component and thus reduces the number of fertilizer granules that contain the micronutrient. The latter factor can be important for elements of limited mobility in soil. Corn forage yields in a greenhouse experiment decreased as the Zn concentration in superphosphate increased from 0.5 to 8% Zn, with the Zn application rate held constant (Giordano & Mortvedt, 1966). The number of Zn-containing granules required to supply 3 mg of Zn was 32, 8, and 2 when the Zn concentration was 0.5, 2.0, and 8.0%, respectively. After movement of Zn from these granules in soil was measured, the volume of soil affected by applied Zn was calculated to be 5.0, 1.2, and 0.3% of the 3 kg of soil in each pot.

Table 12–2. Range in micronutrient concentrations in four bags of granular fertilizers after incorporating ZnO in granular MAP and blending this product with granular KCl and powdered MnO (Hignett, 1964).

	Test 1		Test 2	
Bag no.	% Mn	% Zn	% Mn	% Zn
1	3.0	0.7	2.9	1.4
2	0.7	0.6	0.9	1.6
3	2.9	0.6	9.8	1.1
4	0.6	0.6	4.9	1.4
Intended conc	3.0	0.5	3.0	1.2

Applying granular micronutrients in bulk blends of mixed fertilizers is perhaps the most popular application method. Using granular sources helps prevent segregation from the mixed fertilizer because of more equal particle sizes, but the granule size of micronutrient sources reduces the number of application sites in the soil. For example, the number of granule sites may be $< 20/m^2$ when granular $ZnSO_4$ is applied at a rate of 1 kg of Zn/ha. In contrast, if $ZnSO_4$ were incorporated with a mixed fertilizer to contain 2% Zn, the number of granule sites would be about $350/m^2$ at the same Zn rate. Application of granular sodium tetraborate ($Na_2B_4O_7$) also results in high B concentrations in soil near the granule site, which could be toxic to nearby plant roots (Mortvedt & Osborn, 1965). Granular oxides of micronutrients may not be available to plants because they are relatively water insoluble, and their specific surface is greatly reduced in granule form. Granular ZnO was ineffective in providing Zn for corn (Allen & Terman, 1966), and granular MnO did not provide available Mn for oats (*Avena sativa* L.) (Mortvedt, 1977) in greenhouse tests. Therefore, granular oxides may not be recommended for use in bulk blends, especially to correct micronutrient deficiencies in young plants.

4. Mixing with Fluid Fertilizers

Application of micronutrients with fluid fertilizers generally assures uniform analysis and application. Because it is relatively easy to mix desired amounts of micronutrients with fluid fertilizers just before application, this method of applying micronutrients has become popular in the USA. Clear liquids are used widely as starter fertilizers, and some micronutrients, especially certain Zn sources, are easily applied with these products.

Solubility of metallic micronutrient sources is greater in polyphosphate than in orthophosphate clear liquids. Solubility is higher in 11–16–0 (11–37–0) made from electric furnace superphosphoric acid than in 10–15–0 (10–34–0) made from wet-process superphosphoric acid and is still lower in 8–11–0 (8–24–0) made from an orthophosphate base solution (Table 12–3). Solubility of these micronutrients in polyphosphate solutions is related to pH and polyphosphate content; thus, it may not be possible to achieve these levels in fluids with low polyphosphate contents.

Because of their high solubility, enough B and Mo may be incorporated with fluid fertilizers to correct severe deficiencies at usual fertilizer application rates. However, amounts of Cu, Fe, Mn, or Zn supplied as inorganic sources with fluids may not be sufficient to correct deficiencies. Organic sources may be required to provide adequate amounts with solution fertilizers, but some of these products are not compatible with all fluid fertilizers. A jar test should be made to determine compatibility before any micronutrient source is mixed with a fluid fertilizer.

The amounts of some micronutrients that can be applied with clear liquids at the desired N and P rates are limited. Suspensions may be used if greater amounts of micronutrients are desired. Suspensions have an advantage over clear liquids since complete solution of the micronutrient is

Table 12-3. Solubility of some micronutrient sources in ammonium orthophosphate or polyphosphate solutions (Achorn, 1969; Silverberg et al., 1972).

Micronutrient source	Solubility of micronutrient in		
	Orthophosphate	Polyphosphate	
		Wet-process	Electric furnace
	% element by weight		
$Na_2B_4O_7 \cdot 10H_2O$	0.90	0.90	0.9
CuO	0.03	0.53	0.7
$CuSO_4 \cdot 5H_2O$	0.13	1.13	1.5
$Fe_2(SO_4)_3 \cdot 9H_2O$	0.08	0.80	1.0
MnO	<0.02	0.15†	0.2†
$MnSO_4 \cdot H_2O$	<0.02	0.15†	0.2†
$Na_2MoO_4 \cdot 2H_2O$	0.05‡	0.38‡	0.5‡
ZnO	0.05	2.25	3.0
$ZnSO_4 \cdot H_2O$	0.05	1.50	3.0§

† Precipitates formed after several days.
‡ Largest amount tested.
§ Solution pH of 6.0.

not required. Micronutrient sources of low water solubility, such as oxides, also may be used in suspensions.

Incorporation is done while suspensions are being made or just before application in the field. Particles of micronutrient sources should be fine enough not to settle in the suspension or clog spray nozzles. Particle sizes finer than 60-mesh size are suggested for incorporation with suspensions (Mortvedt, 1979). Incorporating micronutrients with suspensions must be done in a manner to prevent the formation of aggregates, which are very difficult to disperse. One of the best ways to incorporate dry, fine powders directly into suspensions is through use of an injector or an eductor (Silverberg et al., 1972).

II. MARKETING

A. Philosophies of Use

Liming materials are applied to decrease soil acidity, but they also usually supply sufficient Ca and Mg to meet crop needs at optimum soil pH levels. One philosophy of liming is that the soil pH should be increased to about 5.5 to neutralize exchangeable Al^{3+}, whereas others recommend increasing soil pH levels to between 6.0 and 7.0 for optimum crop production. Dolomitic lime should be used, if possible, for liming soils that are low in exchangeable Mg^{2+}; other Mg fertilizers then may not be required to meet Mg needs of crops. Additional Ca is needed for a few crops even though the pH is in the proper range.

The "shotgun" approach has been used to add low amounts of more than one, and sometimes all, micronutrients to the soil. This method, designed to supply all micronutrients removed by a crop, could be considered as an insurance or maintenance program. "Premium" fertilizers containing all micronutrients were promoted in this manner; usually this program did not consider specific crop needs or levels of available micronutrients in soil. Now that soil and plant analyses can more accurately assess micronutrient levels, it is preferable to apply only those nutrients required to reach a specified yield goal for a crop in a given field. This practice helps prevent excessive application of needed micronutrients and eliminates use of those nutrients already present in adequate amounts. More precise recommendations also protect against antagonisms encountered among nutrients in plant nutrition due to unbalanced ratios in soil.

With the development and increased use of bulk-blended granular fertilizers and fluid fertilizers, there is a trend to formulate grades for specific fields at the fertilizer dealer level. These methods increase flexibility in meeting needs and have changed micronutrient marketing methods in the USA.

Manufacturers sell most micronutrients to wholesale distributors or directly to fertilizer dealers, who prepare the requested formulations for farmers at their local plants. A number of granular fertilizers containing micronutrients also are made at NPK manufacturing plants. The premium fertilizers are made for a specific crop over a wide geographic area. For example, a premium fertilizer for corn in the Corn Belt may contain 1 to 2% Zn, 0.5% Mn, and possibly very low amounts of the other micronutrients. Premium fertilizers for soybeans contain higher levels of Mn than Zn, whereas those for cotton (*Gossypium hirsutum* L.) contain mainly B and Mn. Because numerous tons of a specific grade are needed for profitable production, the demand for such a grade must be estimated beforehand.

Foliar sprays containing one or more micronutrients also are sold by many fertilizer dealers. Advantages of foliar sprays are (i) application rates are much lower than for soil application, (ii) uniform distribution is easily obtained, (iii) response to the applied nutrient is almost immediate so that deficiencies can be corrected during the growing season, and (iv) suspected deficiencies can be more easily diagnosed with spray trials. Disadvantages are: nutrient demand is often high when plants are small and leaf surface is insufficient for foliar absorption, leaf burn may result if salt concentrations are high; it may be too late to correct the deficiency and still obtain maximum yields; there is little residual effect from foliar sprays, and extra application costs may be required. It is often convenient to combine a micronutrient with an insecticide or fungicide. Examples include B with an insecticide for cotton and Zn with an insecticide for rice (*Oryza sativa* L.).

Soil and plant analyses are widely used to diagnose nutrient deficiencies. Many fertilizer dealers take soil and plant tissue samples for their customers and have the samples analyzed by university or commercial laboratories. The dealer then discusses the resulting recommendations with the farmer, and they develop a fertilizer plan. Results of several surveys have shown that farmers depend heavily on recommendations made by their local fertilizer dealer. Therefore, much effort is made to educate dealers on the most effective means of providing fertilizers for the farmer.

B. Consumption Data

1. *Liming Materials*

Use of agricultural limestone in the USA was very low until 1935 when new federal soil conservation programs provided financial assistance to farmers for applying lime, and annual lime use increased > 10-fold in 15 yr (Barber, 1967). Since then, it has continued to increase steadily from about 21 million metric tons in 1960 to more than 32 million metric tons in 1980 (Table 12–4). This may be related to more educational programs, better application equipment, and a greater number of lime vendors. A large amount of liming materials now is applied by custom applicators with bulk handling equipment. Increased N use results in an increase in soil acidity, which requires more frequent lime applications. Effects of lime applications are discussed in chapter 4 of this book. Use of gypsum and Mg-containing materials for direct soil application has not increased appreciably since 1970 (Table 12–4). Use of dolomitic lime for soils requiring Mg applications may account for variable consumption of Mg materials since 1960.

2. *Micronutrients*

The Crop Reporting Board of the Statistical Reporting Service of the U.S. Department of Agriculture began publishing summaries of micronutrient use in 1968. Data in Table 12–5 were obtained from the known pro-

Table 12-4. Amounts of agricultural lime, gypsum, and Mg materials used for direct application to soils in the USA.

Year	Lime†	Gypsum‡	Mg materials‡
	1000 metric tons		
1960	21 076	1 300	..
1965	26 439	1 410	4.6
1970	34 423	1 150	1.8
1975	32 262	1 630	3.6
1980	32 648	1 860	5.0

† Levenson et al. (1981).
‡ Statistical Reporting Service (1961, 1966, 1971, 1976, 1981).

Table 12-5. Amounts of micronutrients sold in the USA (Statistical Reporting Service, 1968, 1972, 1975, 1978, 1981).

Year	Cu	Fe	Mn	Mo	Zn
	1000 metric tons†				
1967–1968	2.2	3.1	10.5	0.07	13.1
1971–1972	0.6	1.2	11.2	0.09	14.4
1974–1975	0.5	1.9	10.3	0.13	12.7
1977–1978	1.2	3.9	16.8	0.10	33.1
1980–1981	1.4	6.4	12.7	0.01	39.9

† Amounts expressed on elemental basis.

ducers of Cu, Fe, Mn, Mo, and Zn sources for use in both mixed and direct application in each region of the USA since 1967. Boron use data were not included since there were so few producers of fertilizer B. However, recent reports have estimated 1982 use at 3037 metric tons of B (Lyday, 1982).

Amounts of Cu and Fe used in the USA decreased from 1968 to 1972 and increased thereafter (Table 12–5), but the amount of Cu sold in 1980 still was lower than in 1967. Decreased use of Cu was related to lower consumption in Florida, where recommended rates were decreased. Toxicities to plants can result if Cu levels are too high, especially on acid, sandy soils. Amounts of Zn and Mn are the highest because these micronutrients are recommended for such large-area crops as corn, wheat (*Triticum aestivum* L.), soybeans, and rice. Rapid increases in Zn usage since 1975 are related to actual increases in consumption as well as to the inclusion of more producers reporting Zn sources, including some industrial by-products.

The figures in Table 12–5 are reported on an elemental basis; thus, the actual amount of materials used is much higher. This method of reporting was necessary since the nutrient content of the micronutrient sources varies widely. The tonnage of micronutrient materials sold in this country is only about 1% of the tonnage of NPK materials.

C. Regulations

Fertilizer regulations are governed by each state in the USA. In 1963, a general proposal was made that minimum percentages for the allowable levels of micronutrients be established and guaranteed on fertilizer labels. A uniform state fertilizer bill for general standardization was proposed by the AAPFCO for legislation by each state to simplify interstate shipping of fertilizers. The suggested minimum percentages acceptable for registration of each nutrient are shown in Table 12–6. Control officials emphasized that these were not to be considered as recommended levels; they are simply levels that can be determined accurately in control laboratories. One

Table 12-6. Suggested minimum percentages of secondary and micronutrients that can be guaranteed on a fertilizer label and also allowable deficiencies in fertilizer grades (Assoc. of Am. Plant Food Control Officials, 1968).

Nutrient	Minimum guarantee, %	Allowable deficiency†
Ca	1.00	0.2% + 5% of amount guaranteed
Mg	0.50	0.2% + 5% of amount guaranteed
S	1.00	0.2% + 5% of amount guaranteed
B	0.02	0.003% + 15% of amount guaranteed
Cu	0.05	0.005% + 10% of amount guaranteed
Fe	0.10	0.005% + 10% of amount guaranteed
Mn	0.05	0.005% + 10% of amount guaranteed
Mo	0.0005	0.0001% + 30% of amount guaranteed
Zn	0.05	0.005% + 10% of amount guaranteed

† Percentage of element below the guaranteed percentage on the fertilizer label that is allowed before the element is considered deficient in the fertilizer grade.

disadvantage of allowing such low levels of micronutrients to be guaranteed on fertilizer labels is that these amounts applied to soils at the usual NPK rates are too low to be of much benefit to crops if there are micronutrient deficiencies. Some states have set minimum guarantee levels more in line with their recommended levels of these elements.

This bill also states that such elements shall be deemed deficient in the fertilizer formulation if they are lower than the guarantee on the label by an amount exceeding the values shown in Table 12–6. For example, the allowable deficiency would be 0.205% Zn in a fertilizer grade containing 2.0% Zn. Guarantees and allowances vary by states. Increasing numbers of fertilizers are being offered with a guarantee for micronutrient content. Frequency of deficiencies appears to be in line with those found for the macronutrients.

Another suggestion was that the fertilizer laws require a warning or caution statement on the label for any product containing > 0.03% B or 0.001% Mo in water-soluble form. This is to prevent toxicity of B to the plant through overuse and as a safeguard against Mo toxicity to animals resulting from consumption of forage with a high Mo concentration. To date, 38 states have adopted portions of this bill in their fertilizer laws.

III. METHODS AND RATES OF APPLICATION

The use of secondary and micronutrient fertilizers is governed by principles affecting both the need for and application of these nutrients. Needs are determined by crop requirements and soil conditions, which include amounts of a given nutrient present and reactions that affect their availability to plants. Efficient and effective use of any fertilizer depend on the source, rate, and method of application. Also, the philosophy of whether the crop or the soil is being fertilized must be considered. Soil fertilization with certain nutrients also may result in substantial residual effects, and these need to be evaluated in long-term studies. The focus in this section is on rate and method of application, but sources and time of application also are included as applicable. Major emphasis is on research results published since 1971, and residual effects are discussed briefly.

A. Calcium

The rather large amount of exchangeable Ca^{2+} in the soil that normally dominates the exchange complex satisfies the Ca requirements of most crops. Under acid conditions the amount of exchangeable Ca^{2+} in soil decreases, whereas exchangeable Al^{3+} increases, and Al toxicity may eventually cause reduction in plant growth. Correction of this acid condition is accomplished by liming with either calcitic or dolomitic lime, which maintains an abundant supply of Ca in the soil.

An international symposium on Ca nutrition of economic crops was held in 1977 (Shear, 1979). The proceedings provide excellent information on the nature of the problem and approaches as to correction, especially on horticultural crops.

Calcium deficiencies have been reported in some crops even thoug soil acidity may not have been extreme. Such deficiencies are usually loca ized in fruits, storage organs, or shoot tips—plant parts that are natural low in Ca. Some examples are poor kernel formation in peanuts (*Arachi hypogaea* L.), bitter pit in apples (*Malus sylvestris* Mill.), blossom end ro in tomatoes (*Lycopersicon esculentum* Mill.), tipburn in lettuce (*Lactuc sativa* L.), and black heart of celery *(Apium graveolens)*. Many other ex amples existing in fruits and vegetables have been listed by Shear (1975).

The field crop most likely to show Ca deficiency due to the need for liberal supply of Ca for proper development of its subterranean fruit is pea nuts. Walker (1975) reviewed the Ca requirement of peanuts and reporte lime to be somewhat effective, but the more soluble $CaSO_4$ (gypsum, o "landplaster") was superior. Gypsum is usually applied at 600 to 800 kg/h just before fruiting in a 45-cm band over the row. Only a few definitive studies have been conducted to establish the optimum rate of gypsum fo peanuts. Yield responses likely are mediated by environmental condition and are not guaranteed, even under low soil Ca levels. Furthermore, it ha not been shown that the Ca rate should be increased with decreasing level of soil Ca. Essentially full yield response has been obtained with gypsun rates as low as 200 kg/ha (Cox, 1972), but the recommended rates usuall are higher for several reasons. The yield and grade may continue to in crease with increasing rate of applied Ca; Walker et al. (1979) found this t be true even above 600 kg of gypsum/ha. Thus, it is economical to apply th higher rates because of the increased value of the crop. Adequate Ca also ensures good quality seed that germinate well (Cox et al., 1976), and high Ca rates may help reduce certain forms of pod rot disease (Hallock & Gar ren, 1968; Walker et al., 1979).

The term *gypsum* is used in a general sense to mean a material with a calcium sulfate base. Little pure $CaSO_4 \cdot 2H_2O$ is sold; most commercia sources range from 50 to 90% $CaSO_4$. Textures range from very fine t granular, and some by-product precipitated materials vary in particle size due to lumps forming in the damp material. Because fine materials reac more quickly than coarser materials (Daughtry & Cox, 1974; Keisling & Walker, 1978), fine materials may have an advantage for peanuts if applie at the typical early flowering stage. Coarser materials are often applied by bulk spreading very early in the growing season, which is the only perio when such equipment may be used without damaging plants. All materials seem to be effective (Hallock & Allison, 1980), but the broadcast rate must be about twice the banded rate due to the extra material that covers the area between the rows.

Although generally considered less effective than gypsum, limestone was a satisfactory source of Ca for 'Florunner' peanuts (Adams & Hartzog, 1980). The rate needs to be higher than that for gypsum (Adams & Hartzog, 1979), and lime must be incorporated at a very shallow depth to affect primarily the fruiting zone in the soil. Sullivan et al. (1974), however, found this treatment completely ineffective with cv. NC5.

Foliar applications of Ca are not effective with peanuts since there is little xylem flow to carry the nutrient to the developing fruit. A similar

problem exists with head lettuce. Misaghi et al. (1981) found foliar sprays of either calcium chloride ($CaCl_2$) or calcium nitrate [$Ca(NO_3)_2$] ineffective in reducing tipburn incidence and severity. The deficiency occurs on the inner and middle leaves, which are not exposed after head formation. Soil applications of $Ca(NO_3)_2$ were not effective, but $CaCl_2$ at 224 kg/ha or greater increased tissue Ca and reduced tipburn in one of six trials.

Among the horticultural crops showing Ca deficiency, apples have been studied most extensively. Recently, Lidster et al. (1978a, 1978b) studied effects of prebloom and summer foliar applications of Ca as well as a postharvest dip of the fruit in reducing breakdown development in stored 'Spartan' apples. They found prebloom $CaCl_2$ sprays to be ineffective, but summer sprays (0.6% $CaCl_2$) applied four times at 2-week intervals beginning in mid-July increased fruit Ca levels and decreased breakdown development significantly. A postharvest dip in 4% $CaCl_2$ was even more effective, but the most effective method was to combine summer sprays with the postharvest dip.

Application of lime and minimizing the K supply have been used to reduce Ca deficiency, termed *metsubure*, in taro [*Colocasia esculenta* (L.) Schott] corn (Tanabe & Ikeda, 1980, 1981). Both treatments affected the K/Ca ratio in the corms. There was no effect of N source as sometimes occurs with other crops, but varietal differences were noted. There appears to be great potential to develop varieties for tolerance to low Ca conditions for this crop as well as for many others.

B. Magnesium

Availability and plant uptake of Mg, like Ca, decreases under acid soil conditions due to a pH effect and also due to the direct loss of Mg from the root zone. Increasing the pH of a soil, even with a calcitic source of lime, often increases the uptake of Mg (Christenson et al., 1973). However, the primary method to ensure an adequate level of Mg in acid soils is by applying dolomitic lime. This has been the dominant source of Mg, even in the South Atlantic states, where Mg deficiencies should be most severe. The most common fertilizer sources of Mg are MgO and the sulfate form, usually applied as potassium sulfate–magnesium sulfate ($K_2SO_4 \cdot MgSO_4$).

The status of Mg research in the southeastern USA as well as factors affecting the availability of Mg to plants and animals were discussed in a symposium in 1972 (Jones et al., 1972). Grass tetany, a Mg deficiency occurring during lactation in ruminant animals, is the most important problem associated with Mg nutrition. Some low Mg levels in plants also were noted, but most of these were predictable by soil test data. Research results indicated only a small number of yield responses to Mg fertilization.

Soil test interpretations may have changed somewhat since that symposium was held in 1972. At that time, only one state based Mg availability on the cation saturation ratio in soil. This method is becoming more popular, but little substantiating field research has been published. In greenhouse work, McLean and Carbonell (1972) found that 6 to 10% Mg saturation was an adequate level for most Ohio soils, whereas $< 5\%$ Mg saturation is considered deficient and $< 10\%$ is low in North Carolina.

General recommendations for Mg based on soil tests are to use dolomite if lime is needed or Mg at 20 to 40 kg/ha if it must be applied in NPK fertilizers. There have been no recent studies, however, to verify these recommendations. Gallaher et al. (1975) in a 3-yr Mg rate study with grain sorghum [*Sorghum bicolor* (L.) Moench], found a positive yield response the first year, a trend in the second, and no response in the 3rd yr. The maximum Mg rate (68 kg/ha as $MgSO_4$) was required the 1st yr and only 34 kg/ha the second. Klein et al. (1981) reported that 44 kg/ha of $MgSO_4$ was the optimum rate for potatoes (*Solanum tuberosum* L.). This rate had little effect on yield but improved quality by reducing discoloration, which was associated with lower amounts of phenols and more lipids and phospholipids in the tubers. Jones and Jones (1978) compared $MgSO_4$ with dolomite at 20 kg of Mg/ha for tomato production. Yields were increased by both sources in one of three crops, but the sulfate form was more effective than dolomite in increasing leaf Mg in all crops.

Application of $MgSO_4$ does not always increase tissue Mg concentration appreciably. In three Mg rate studies in Kansas, corn leaf Mg levels at silking ranged from 0.10 to 0.12% and showed little response up to 270 kg/ha of Mg as $MgSO_4$ (Whitney, 1973). Lack of a response seemed to be associated with very high Ca activities in these soils.

C. Boron

Sodium tetraborate is the main source of fertilizer B. Levels of hydration among the materials available result in B concentrations ranging from 11 to 20%. The most concentrated form is especially adapted for foliar sprays. Boron may be applied to either the soil or the foliage to correct a deficiency; Gupta and Cutcliffe (1978) found both methods to be effective in controlling brown heart in rutabaga (*Brassica napobrassica* L.). Several foliar applications at a low rate were more effective than a single application at a higher rate; this has been shown with other crops and is apparently due to the immobility of B in leaf tissue (Anderson & Ohki, 1972).

The rate of B required to correct a deficiency in annual crops is low. Murphy and Lancaster (1971) obtained maximum cotton yields with either 0.5 kg of B/ha applied to the foliage (fives times at 0.1 kg/ha each) or > 0.3 kg/ha applied to soil. Hill and Morrill (1974) found a similar rate sufficient to maintain the quality of peanuts; B could be applied any time up to 60 d after planting and still be effective for that crop. Rates > 1.0 kg/ha may create B toxicity. Blamey and Chapman (1979) noted yield reductions even before observing B toxicity symptoms in peanuts when high rates were applied to a sandy loam. Rates of 2 to 3 kg/ha are typically applied to alfalfa (*Medicago sativa* L.) when grown on finer-textured soils.

D. Chlorine

Although Cl is readily leached from surface soils in regions of high rainfall, its supply is usually replenished by applications of potassium chloride (KCl), the predominant K source. In regions of low rainfall, Cl may

accumulate. Deficiencies of this element, therefore, are very rare, and it is much more common to find effects of excess Cl. Toxicities of Cl may reduce crop yields, especially under saline conditions. Very high levels of Cl are more likely to affect crop quality than yields under nonsaline conditions. An example of an affected crop is flue-cured tobacco (*Nicotiana tabacum* L.). A high tissue level of Cl is undesirable, because it is associated with a reduction in the burn rate and high moisture equilibrium values. Ishizaki and Akiya (1978) reconfirmed this relationship but also noted that the Cl limit for acceptable burning quality decreased with increasing K concentration.

E. Copper

Factors affecting use of Cu have been reviewed recently in a symposium on Cu in soils and plants (Loneragan et al., 1981). Rates, methods, and sources of Cu for application were discussed by Gartrell (1981) and Gilkes (1981). Even though soil and foliar applications are both effective, soil applications are more common, with recommended rates ranging from < 1 to > 20 kg of Cu/ha. The placement geometry of applied Cu is important; if the Cu source is concentrated and the granules large, few roots have access to the applied Cu. Unless applied Cu is mixed with soil, it may not be available to plant roots, especially if the surface soil remains dry. Efficiency is increased by applying Cu either in solution or as a fine material and either banding or thoroughly incorporating it.

Broadcast applications were more effective than band applications of Cu in increasing the yield and leaf Cu concentration of cucumbers (*Cucumis sativus* L.) (Navarro & Locascio, 1980). A rate of only 2.2 kg/ha increased yields from 11 to 21 metric tons/ha. Barnes and Cox (1973) applied Cu in solution over dormant wheat during the winter and found 3 to 6 kg of Cu/ha to be adequate, even on soils of high organic matter content. These are typical rates and have substantial residual effects.

Foliar application of Cu in solution will cause leaf burn on growing tissue, such as wheat that has broken dormancy. However, damage is minimal, and the treatment is effective if the Cu rate is kept low (0.25–0.5 kg/ha). For higher rates, hydrated lime is added to form a suspension. Basic suspensions or dusts also have been applied to seed with some success, but neither the foliar nor the seed treatment has an appreciable residual effect.

The most common Cu source is copper sulfate ($CuSO_4$). Several studies have compared the effectiveness of several Cu sources, but no differences have been found (Gilkes, 1981; Barnes & Cox, 1973).

F. Iron

Iron deficiencies occur on high pH soils. This condition also may be aggravated by application of alkaline irrigation water. High bicarbonate levels intensify Fe deficiencies, and soil applications of Fe as sulfate sources at rates similar to those for other micronutrients have not been effective. Westfall et al. (1971) found ferrous sulfate ($FeSO_4$) and ferric sulfate [$Fe_2(SO_4)_3$] equally effective for rice production, with rates of 50 to 100 kg of Fe/ha required for maximum yields. Patel et al. (1977) obtained no increase in rice yields from 40 kg of Fe/ha as $FeSO_4$, whereas other treatments were effective. Thomas and Mathers (1979) reported that farmyard manure was more effective than $FeSO_4$ in correcting Fe chlorosis of grain sorghum on a calcareous, Fe-deficient soil.

Other approaches used to increase Fe uptake and utilization are acidulation of the soil, complexing of the Fe by an organic ligand or polyphosphate, and application of gypsum. Acidulation corrected Fe deficiency in paddy rice (Patel et al., 1977), but this approach may not be practical in highly calcareous soils due to the enormous quantities of S required. A modification of this approach was tried by Wallace and Mueller (1978), who found that spot acidulation of as little as 0.4% of the calcium carbonate ($CaCO_3$) under soybean seedlings prevented Fe chlorosis.

Some of the response with soil acidulation may be due to increased S availability rather than increased Fe availability. Dungarwol et al. (1974) found that both acidulation of the soil with S and spraying the plants with a 0.1% H_2SO_4 were effective in correcting chlorosis and increasing yields of peanuts. These treatments increased leaf S and decreased leaf Fe. Leaf Fe was very high, however, and the authors postulated that the treatments increased the activity of Fe in the plant.

Organic Fe chelates or natural organic complexes are used to maintain Fe in an available state for a longer period. The most stable, and thus most successful, of these has been FeEDDHA. Low rates of this chelate have been effective in peanut production (Hartzook et al., 1971) but only if banded 40 to 50 d after emergence. Moraghan (1979) also was able to correct a Mn/Fe imbalance in flax (*Linum usitatissimum* L.) with an application of FeEDDHA. However, Westfall et al. (1971) found low rates of FeEDDHA less effective than high rates of $Fe_2(SO_4)_3$ for rice.

Complexing with polyphosphate fertilizers also increases the availability of fertilizer Fe. Mortvedt and Giordano (1971) showed this effect with both sulfate and chelated Fe sources, but FeEDDHA was more effective than $FeSO_4$ or $Fe_2(SO_4)_3$ at the same Fe rates.

The use of gypsum to increase Fe uptake under greenhouse conditions has been reported by Olsen and Watanabe (1979). Low plant Fe has been associated with high Mo. Gypsum applications decreased plant Mo considerably and increased plant Fe slightly in grain sorghum. This effect may account for part of the beneficial effect of gypsum noted on alkaline soils.

Because of difficulties in correcting Fe deficiencies by soil treatments, other methods generally are used. Foliar applications of Fe with about 3% $FeSO_4$ solution have been effective on some crops. Seeliger and Moss (1976) found a good response with peas (*Pisum sativum* L.) sprayed twice at 3-week intervals. In contrast, Patel et al. (1977) found that foliar-applied $FeSO_4$ was ineffective for rice.

Genetic variation also is used to overcome the problem of Fe deficiency. Hartzook et al. (1974) found that yields of Fe-efficient cultivars of

peanuts were just as high as those of inefficient cultivars that were fertilized with FeEDDHA. This approach should be exploited for many other crops.

G. Manganese

Manganese deficiencies occur on high-pH soils and also on soils which are inherently low in Mn. The degree of Mn deficiency primarily affected by the above factors are seldom considered when the proper rate and method of Mn application are selected. For example, a case of extreme deficiency was found by Reuter et al. (1973), who studied means of correcting Mn deficiency on a soil containing > 8% $CaCO_3$. Manganese applied to the soil increased yields, with 6 kg/ha being as effective as larger rates. Yet deficiency symptoms reappeared late in the season, and a foliar application resulted in a further increase in yields. Apparently, the soil treatment was not effective for the entire period because of oxidation to unavailable forms, and a combination of methods was needed to achieve maximum yields. However, most Mn deficiencies are not as severe as the above and can be corrected by either soil or foliar applications. Even so, because the deficiency still affects the rate of Mn required for correction, recommended rates will not always be the same.

The rate of Mn required to correct a deficiency depends on the method of application, with increasing rates required for foliar, banded, and broadcast applications, respectively. Alley et al. (1978) obtained maximum soybean yields with 2.2 kg/ha foliar, 5.6 kg/ha banded, and 11 to 22 kg/ha broadcast applications on an Atlantic Coastal Plain soil, with the optimum broadcast rate depending on soil pH. Except for lower foliar rates, similar results were obtained by Randall et al. (1975), with maximum yields at 0.56 kg/ha banded and 17 kg/ha broadcast applications. In both of these studies the lowest foliar rate examined was effective; therefore, the actual minimum rate is unknown. Alley et al. (1978) split their foliar rate and found two applications to be more effective than one, but Boswell et al. (1981) found no differences when Mn was applied as broadcast preplant, banded at planting, sidedress, or broadcast preplant plus foliar spray. Soybean yield responses occurred in only 1 of 3 yr and maximized at 11 kg of Mn/ha. In an adjacent study on the same soil, Shuman et al. (1979) reported responses to broadcast preplant Mn in 2 of 3 yr. Soybean yields were highest at the 5.6-kg rate one year and at 11.2 kg the other. Differences among years appeared related to soil test Mn level.

Shuman et al. (1979) also reported that effectiveness of soil-applied Mn sources decreased in the order $MnSO_4$, manganese oxide (MnO), a Mn frit, and then a chelate that was ineffective. Voth and Christenson (1980) obtained similar results with sugar beets (*Beta vulgaris* L.), soybeans, and navy beans. Likewise, Knezek and Davis (1971) obtained good responses to $MnSO_4$ and MnO but emphasized that the particle size was important, especially for MnO, which must be finely ground to be effective.

Mixing or blending Mn sources with certain fertilizers also may increase availability of Mn. Mortvedt and Giordano (1975) found increased Mn uptake by oats when either $MnSO_4$ or MnO was mixed with phosphate

fertilizers. In general, granular phosphates were more effective Mn carriers than fluid polyphosphates. Voth and Christenson (1980) noted that acid-forming fertilizers not only increased availability of fertilizer Mn but also increased that of native soil Mn.

H. Molybdenum

Plant availability of Mo, unlike that of other micronutrients, decreases with increasing soil acidity. Thus, liming to correct acidity improves Mo nutrition of plants. Another condition affecting Mo availability is the Fe status of soil. Soils that are high in Fe, especially noncrystalline Fe on clay surfaces, tend to have lower levels of available Mo.

The optimum Mo rate depends on the application method. Molybdenum may be applied to soil, sprayed on foliage, or put on seed prior to planting. The application rate is very low, especially for the latter two methods. Parker (1978) found that about 1 kg of Mo/ha was needed for soybeans if it was band applied before planting, but only 25 g/ha was required for either foliar or seed applications. Their foliar spray was split into two applications. Other work (Boswell & Anderson, 1969) has shown that foliar sprays of Mo should be applied prior to the bloom stage.

Legumes are especially sensitive to Mo deficiency, but the deficiency symptoms exhibited are those of N deficiency. Parker and Harris (1977) found that the primary function of Mo for soybeans was to correct N deficiency; there was enough soil Mo for nitrate reduction, but not enough for the rhizobial symbiont. They used both seed and foliar treatments at 17 to 34 g of Mo/ha.

Giddens and Perkins (1972) studied the response of alfalfa to Mo applications on two highly oxidized Piedmont soils, a Typic Hapludult and a Rhodic Paleudult. They obtained responses to 100 g of Mo/ha even though the soils were limed before planting each year during the study.

Obtaining uniform distribution of small rates applied to soil is difficult. Giddens and Perkins (1972) applied to Na_2MoO_4 as a solution to broadcast it uniformly. In Australia, molybdenum trioxide (MoO_3) has been incorporated into phosphate rock pellets to facilitate distribution. Kerridge et al. (1973) found this technique as effective as a direct application of MoO_3 at 100 g of Mo/ha for pasture legumes. Another method is to incorporate MoO_3 in a seed pellet. Johansen et al. (1977) found no difference among methods when Mo was applied in a seed pellet or to the soil surface as MoO_3 or Na_2MoO_4 for pasture legumes. They also found the Mo requirement among several sites varied from nil to 200 g/ha, and one application was effective for 3 yr. This study also confirms earlier observations that there are no differences among commonly used Mo sources.

Several interesting interactions concerning the Mo nutrition of burley tobacco have been studied. This crop usually is grown under acid soil conditions and may receive rather heavy applications of sulfate in the fertilizer. Sims et al. (1979) found that application of sulfates tended to reduce yields at low soil Mo levels but increased yields at high soil Mo levels. Sims and Atkinson (1976) found that applied Mo may be rendered partially un-

available in a soil of pH < 5.4, because there was a positive response to Mo fertilization when the soil was limed. These studies also indicated that soil application of about 0.5 kg of Mo/ha applied to the soil was adequate.

I. Zinc

Zinc has been applied to both soils and plants by several methods. Soil application methods include broadcast incorporated, surface broadcast, and banded. Plant methods include seed coatings, root dips, and foliar sprays. Several sources of Zn are sold—sulfate, oxide, chelates, natural organic complexes, and frits—and a number of options are available to correct Zn deficiencies.

For corn production, soil application of Zn has proved more effective than plant methods. Tanner and Grant (1973) found soil fertilization more effective than seed coatings, and Grewel and Singh (1975) found a similar trend when comparing soil and foliar applications. Hawkins et al. (1973) found that disked-in and plowed-down $ZnSO_4$ were equally effective, and the optimum Zn rate was 6.7 kg/ha. Maximum yields with broadcast $ZnSO_4$ in a regional study were obtained with 3 to 9 kg of Zn/ha (Cox & Wear, 1977). Schnappinger et al. (1972) broadcast both $ZnSO_4$ and ZnEDTA in solution prior to incorporation and found 14 kg of Zn/ha as the optimum rate with $ZnSO_4$; the highest rate of ZnEDTA (4.4 kg of Zn/ha) was not sufficient for maximum corn yields.

Considerable research also has been conducted on Zn deficiency of rice. Randhawa et al. (1978) estimated that about 2 million ha of rice soils in Asia are believed to be Zn deficient. For paddy rice, Yoshida et al. (1973) found that dipping transplant roots in a 1 to 2% ZnO suspension was effective in controlling Zn deficiency. Mikkelson and Brandon (1975) found ZnO somewhat less effective than $ZnSO_4$, but ZnO was still economical due to its lower cost. An effective rate for both sources was about 8 kg/ha. In contrast, Amer et al. (1980) reported that ZnO was superior to $ZnSO_4$ and that 5 kg of Zn/ha was sufficient for rice in Egypt. In the two reports just cited, applying Zn to the soil surface before flooding or to the surface water after transplanting were equally effective.

Zinc chelates are effective for rice production (Kang & Okoro, 1976) as well as navy bean and corn production. Boawn (1973) concluded that only about half as much Zn was required for corn and beans if ZnEDTA was the source rather than $ZnSO_4$. Results indicated that ZnEDTA might be applied effectively through sprinkler irrigation, but little response would be expected from $ZnSO_4$ applied in this manner. This hypothesis is supported by the work of Halvorson and Lindsay (1977), who suggested that chelation aids in the transport and movement of metal ions to plant roots.

The optimum method, source, and rate of Zn application varies for other crops as well. For wheat, Trehan and Sekhon (1976) obtained maximum response with about 3 kg of Zn/ha banded or 9 kg/ha broadcast as $ZnSO_4$, but Zn frits were less effective. Tehran and Grewel (1981) reported that dipping potato tuber pieces in a 2% ZnO suspension gave greater increases in yield and tuber size than several other methods. Foliar sprays have been used effectively with grapes (*Vitis vinifera* L.) (Christenson, 1980) and pecans [*Carya illinoensis* (Wangenh.) K. Koch] (Smith et al., 1979) but only when applied at certain times or in a particular manner. For pecans an aerial application was not effective even though the foliar rate was 6 kg of Zn/ha.

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soils require special management. Acid sulfate soils not only have active acidity that must be dealt with, but have reserves of pyrite that can generate large amounts of acid under drained conditions. In alkaline soils, micronutrient availability, especially Zn and Fe, are frequent problems.

Lime may be applied to excessively acid soils to improve fertilizer use efficiency, supply Ca and/or Mg, enhance the mineralization of organic matter and release of NH_4^+–N, to favor N_2 fixation by blue-green algae, reduce metal toxicity, and to favor a rotation crop. Excessive liming should be avoided, since it reduces the availability of most micronutrients, except Mo. Liming alone is usually not a feasible treatment for acid sulfate soils because the very high potential acidity can neutralize very large amounts of lime.

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7

Production, Marketing, and Use of Nitrogen Fertilizers

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I. NITROGEN IN NATURE

A. The Nitrogen Resource

Large quantities of free N are found in the atmosphere, which is about 80% N by volume. Although this abundance of N exists, it cannot be used by higher plants until it is combined with hydrogen (H_2) or oxygen (O_2). If inexpensive methods were available to produce these combined N compounds, the problem of supplying adequate N for crop production would be simplified. However, much energy and expense are required to fix atmospheric N.

Substantial quantities of N also occur in chemically combined forms in soils, geologic formations, and oceans. Nitrogenous compounds may be either organic or inorganic. Some nitrogenous compounds, like the elemental dinitrogen (N_2) are gaseous but the most important compounds in agriculture are nitrate (NO_3^-) and ammonium (NH_4^+).

Of the six known isotopes of N, only those having mass numbers of 14 and 15 are stable and occur naturally. The isotope of mass 13 is the longest lived of the four radionuclides, with a half-life of 10.05 min. This relatively brief half-life is too short for practical use in most research on biological systems. The stable N isotopes (^{14}N and ^{15}N) have been used almost exclusively as tracers for biological and related types of research, because the two occur naturally in an almost constant ratio (^{14}N to ^{15}N is about 272:1).

The ^{15}N tracer technique is more accurate than the older methods of N recovery, which consider the difference between N removed from control

soils by the crop and that removed from fertilized soils. The tracer method is based on actual recovery of added ^{15}N in the crop plus that remaining in the soil. These techniques are expanding our understanding of the fate of N, especially as related to its use for crop production. However, there remains many unanswered questions relative to optima N production, marketing, and use.

B. Role of Nitrogen in Plants

Established as an essential mineral element for rooted plants in the 1800s, N has been recognized to be responsible for lush vegetative growth and a dark green leaf color. Its deficiency is usually recognized first by the pale green or yellowish-green color, especially in the grasses, and the premature necrosis of the older leaves beginning from the tip and progressing along the midrib toward the collar and the edges. This association with green coloration is likely due to the fact that N, along with Mg, is one of two soil-derived constituents of chlorophyll ($C_{33}H_{72}O_5N_4Mg$). Adequate N for plants promotes aerial vegetative growth, increases the top/root ratio, and is essential for fruit and seed formation. Being an essential constituent of amino acids, N is required in protein synthesis, making up 12 to 19% of various proteins and averaging about 16% by weight. Because grain formation depends on certain threshold levels of protein, grain production is significantly related to N supply, especially in cereal crops. Abundance of N in the growth medium also is reflected in the crude protein levels of grain and in forages. Among the essential mineral elements for the growth and reproduction of higher green plants, there are more atoms (approximately threefold) of N in dry organic matter than of any other soil-derived element (not from water or the atmosphere). In terms of mass, N in plant material is often found in larger quantities than any other element. Although the concentration of K may be higher in some plant materials, N exceeds the combined total of all other soil-derived essential mineral elements in the seeds of commonly grown agricultural crops.

Considering the abundance of N in plants, its central role in plant functions and its reactivity in the biosphere, it is not surprising that this element is the most universally deficient for optimum crop production.

C. Dinitrogen Fixation in Nature

Rooted green plants may absorb N in several combined forms and through different organs, but the preponderance is usually absorbed through the roots in ionic form either as NH_4^+ or NO_3^-. Some plants can absorb and utilize only NH_4^+, but most do absorb both ions; the ion absorbed depends more on the environment than on plant capability. Hence, rice (*Oryza sativa* L.) grown under flooded conditions is most likely to absorb its N as NH_4^+, and maize (*Zea mays* L.) grown in well-aerated soils will absorb mostly NO_3^-. Also, NO_3^- is likely to predominate as the absorbed form in late spring and summer when aerated soils are warm, resulting in N transformation to the NO_3^- form.

Because rooted plants cannot utilize gaseous N, they must have a su ply of combined N for growth. There are a number of processes in natu that convert N_2 to forms useful for plants; some involve living organism while others are independent.

1. Lightning

Electrical discharges related to meteorological events fix a certa amount of N in the atmosphere. The products are most likely to be nitrog nous oxides. This direct oxidation of N by electrical discharge, demo strated by Cavendish, was the basis for early attempts at commercial pro esses for producing combined N. The reactions may be shown as follows:

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO.$$

Precipitation washes these compounds from the air, along with variou other organic and inorganic forms of N originating as atmospheric intru sions from activities near the earth's surface. Thus, it is not possible to de termine the importance of direct oxidation by lightning. The amount of N deposited annually in precipitation varies among location, with 10 kg/h being about the average value. This is not nearly enough N for high yield of most crops.

2. Fixation by Organisms

Organisms that can utilize free N directly (i.e., fix it) may be divided into two classes—symbiotic organisms and free-living organisms. Symbiotic organisms can function only in symbiotic relationships with a rooted green plant; free-living organisms function independently, usually depending only on a fixed energy source. The blue-green algae, however, are even independent of fixed energy because of photosynthesis in these lower green plants. There are at least 12 kinds of blue-green algae that have this capability. This is emphasized because algae are often implicated in eutrophication of lakes and streams due to nutrient enrichment of the water. It is evident that the blue-green algae can multiply in waters without N enrichment.

Besides the blue-green algae, *Rhodopseudomonas*, *Thiodomusbium*, *Chlorobium*, and *Chromatium* also are autotropic and fix N_2. These organisms need certain essential elements, light, CO_2, and N_2, for growth and N_2 fixation.

The other free-living organisms that can fix N_2 are saprophytes, i.e., they require an external energy source to grow and to fix N_2. Like the others, these require essential elements for growth but tend not to fix atmospheric N_2 when N sources, especially NH_4^+, are readily available in the growth medium. Some of these such as *Clostridium* sp. and *Aerobacter* sp. are anaerobic, while others like *Azotobacter* sp., *Achromobacter* sp., and *Beijerinckia* sp. are aerobic.

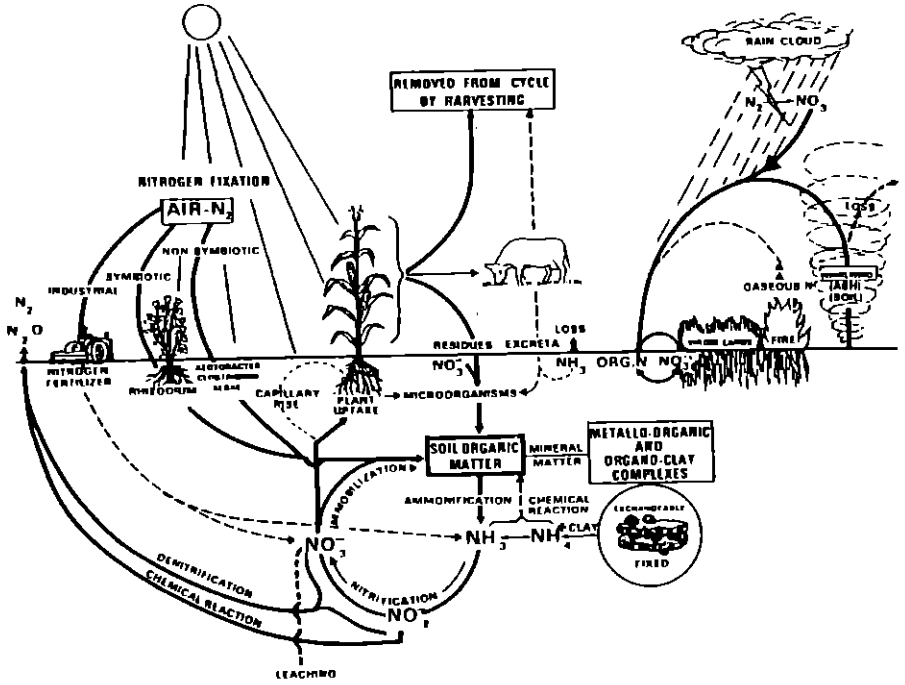


Fig. 7–1. The nitrogen cycle (courtesy of Stevenson, 1964).

D. The Nitrogen Cycle

A graphic portrayal of the relationship of the various forms of N in nature is given in Fig. 7–1. It shows the two larger reservoirs of N mostly as N_2 in the atmosphere and as combined N in the soil and other parts of the earth's crust.

The use of the latter of the two reservoirs is conditioned by its location, time, and usually by the presence of higher green plants; a very small portion, however, is found in deposits that are exploited for fertilizer and other uses. Atmospheric N, on the other hand, is quite uniformly distributed over the earth and it can be fixed favorably, either by the physiochemical processes described later in this chapter or by growing leguminous species of higher green plants. Dinitrogen fixation by organisms nonsymbiotically and naturally by lightning is not yet controlled adequately for general use; however, this N is significant for producing food, feed, and fiber under native conditions.

Regardless of various ways that N may be added to the soil, it often undergoes many transformations before it is removed. Organically combined N is subjected to complex changes such as protein formation and decomposition. Nitrogen also appears in forms that can be appropriated by microorganisms and higher plants, immobilized and slowly released by mineralization, lost by volatilization, leached in the NO_3^- form, and/or removed by erosion. These processes serve to utilize, recycle, or lose N from the soil-crop system.

II. COMMERCIAL DINITROGEN FIXATION PROCESSES

Nitrogen fertilizer production capacity and use have increased tremendously throughout the world since about 1975. A number of obsolete ammonia (NH_3) plants have been replaced with new modern plants and other old, high-production cost plants have been shut down.

The basic processes have changed little from the original means of synthetically producing anhydrous NH_3, the starting product for nearly all N fertilizers. The reactions are the same and only variations in pressure, temperature, catalyst, mechanical equipment, and gas purification distinguish the different commercial processes available or in operation (Axelrod & O'Hare, 1964; Sauchelli, 1960, 1964). Significant economic improvements have been realized in modern plants by the use of heat interchange throughout the various process steps and by the use of centrifugal compressors. Advances in technology, metallurgy, mechanical equipment design, and instrumentation have made possible the modern single-train manufacturing facility. The application of centrifugal compressors has been one of the chief factors in the development of today's single-train plant; it is not uncommon to find one centrifugal compressor doing the work formerly done by 30 to 40 reciprocating compressors. Advances in metallurgy have brought about much higher pressure steam-hydrocarbon reformers, which have greatly reduced the investment in new single-train plants.

A. Ammonia

Anhydrous NH_3 is the basic building block for almost all synthetic N fertilizers. Formula, molecular weight, and physical properties are as follows:

Formula	NH_3
Percent N (by weight)	82
Molecular weight	17.03
Critical temperature	132.4°C
Critical pressure	11.26 MPa
Heat of vaporization (−33.33°C)	1061 cal/g
Liquid density (0°C)	637.8 g/L
Vapor density (0.101 MPa, 0°C)	0.7708 g/L
Boiling temperature (0.101 MPa)	−33.3°C
Freezing temperature (0.101 MPa)	−77.7°C

Gaseous NH_3 is lighter than air, but on compression and cooling it becomes a liquid about 60% as heavy as water. It is readily absorbed in water up to concentrations of 30 to 40% by weight, with the resulting liquid of low

vapor pressure. Due to the high vapor pressure of anhydrous NH_3 at normal temperatures, it is transported in pressure containers. Gaseous NH_3 is extremely irritating to the eyes and respiratory system in concentrations up to 0.07% by volume. A concentration of 0.17% causes convulsive coughing, and concentrations of 0.5 to 1.0% are rapidly fatal after short exposure. While NH_3 does not sustain combustion, it will burn in the presence of air or oxygen if a source of ignition is present, but combustion will stop when the source of ignition is removed. The ignition temperature is around 650°C. Flammable and explosive mixtures are formed with air in concentrations of 16 to 25% NH_3 by volume.

1. Synthetic Ammonia Processes

All processes used are basically modifications of the original Haber-Bosch process in that the NH_3 is synthesized from a 3:1 volume mixture of H and N at elevated temperature and pressure in the presence of an iron catalyst. The H may be obtained from water, natural gas, oil, or coal, and all the N used is obtained from air. Other than the source of H, the major differences in the various processes used are the manner in which N is obtained from the air, the method employed to purify intermediate gas streams, and the synthesis converter operating pressures. With one or two exceptions, the arc process, the cyanide process, the nitridic process, and the cyanamide process have all faded into obscurity. The manufacture of NH_3 can be broken down into three steps: synthesis gas production, purification, and NH_3 synthesis. Synthesis gas preparation involves the production of a raw hydrogen gas and the addition of the stoichiometric amount of N. Purification comprises the removal of CO_2 and CO, which are synthesis catalyst poisons. Synthesis constitutes the catalytic reaction of N and H at elevated temperature and pressure. The manufacture of NH_3 involves the handling of three simple materials: natural gas, steam, and air. In those parts of the world where natural gas is not yet available, it is replaced by naphtha or other hydrocarbons and the process is only slightly more involved. Refinery gas and cokeoven gas may also be used as the raw H source for NH_3 synthesis. A simplified flow diagram for a modern single-train ammonia plant is shown in Fig. 7–2.

2. Synthesis Gas Production

a. Hydrogen Manufacture—The steam-hydrocarbon reforming process is now the most widely used method of generating H, and natural gas is the most popular and the preferred hydrocarbon feedstock. All traces of S must be removed from any hydrocarbon feedstock before the reforming step can take place, because S is a reforming catalyst poison.

After desulfurization, the feed gas is mixed with superheated steam, preheated to 315 to 425°C, and passed through tubes filled with nickel catalyst in a fired furnace. The reactions that take place between the steam and hydrocarbon are shown below for methane (CH_4), the principal component in a natural gas feedstock (the first reaction shown is by far the most predominant and is highly endothermic):

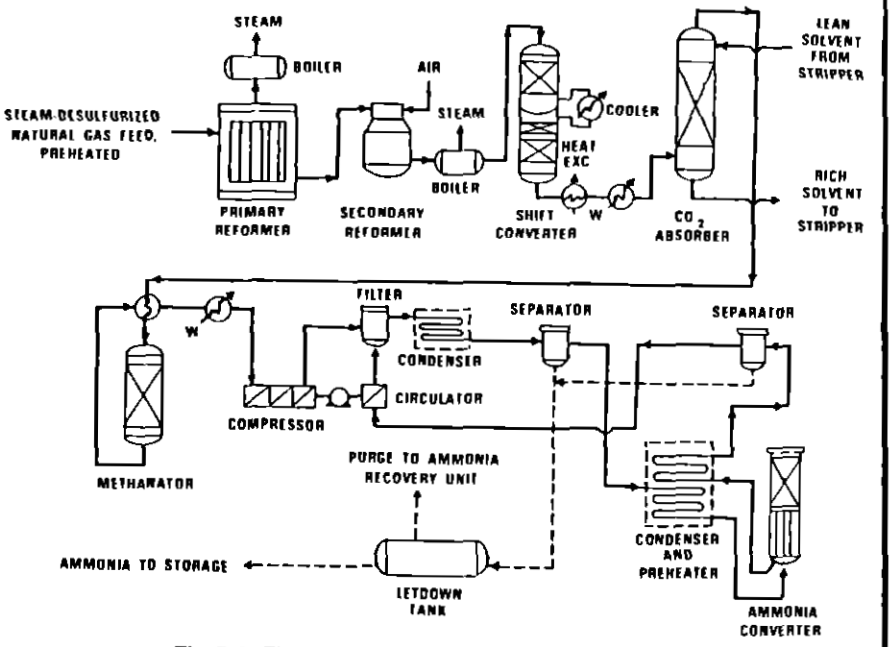


Fig. 7–2. Flow diagram for ammonia synthesis plant.

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

The effluent gas stream from the primary reformer will usually contain enough unconverted hydrocarbon to justify further reforming. This is accomplished by passing the gas over another bed of nickel catalyst. Compressed air is injected into the gas stream entering the secondary reformer. The combustion of the oxygen in this air with a part of the H in the process stream provides the heat required for the reforming reaction, and the noncombustible N component of this air gives the N required to be catalytically fixed with the remaining H to form NH_3.

Partial oxidation is probably the second most popular process for the manufacture of a raw gas for NH_3 synthesis. In this process hydrocarbons are oxidized under pressure to produce a gas that contains H and oxides of C. The reaction takes place in a refractory-lined combustion chamber at temperatures up to 1480°C. Oxygen or oxygen-enriched air is required for this process. The reaction products are cooled and scrubbed to remove C and are then ready for the next step of synthesis gas production.

b. Shift Conversion—The water–gas shift reaction presents a convenient and economic way in which to react or remove CO, which is a synthesis catalyst poison. The raw H stream is cooled to about 370°C, the steam content is adjusted if necessary, and the gas is then passed over an iron-chrome catalyst where the following reaction takes place:

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

The economic advantage to this step is the fact that an additional mole of H_2 is produced for each mole of CO shifted. The removal of the additional mole of CO_2 that is formed is a relatively simple step. In modern plants CO conversion usually takes place in two steps. The first step, which is described above, is exothermic. The exit gas is cooled or quenched to about 200°C and is then passed over a copper–zinc catalyst. The first catalyst bed reduces the CO content of the gas to 2 to 3% by volume and the second catalyst bed further reduces the CO content to the range 0.2 to 0.5% by volume. These two reactions are commonly referred to as high and low temperature shift conversions. The low temperature shift catalysts have been developed since about 1975.

3. Purification

Oxygen will poison the synthesis catalyst and cause it to decrease in activity. For this reason, CO and CO_2 must be removed.

a. Carbon Dioxide Removal—Scrubbing with monethanolamine (MEA) and with hot potassium carbonate (K_2CO_3) are two processes used for CO_2 removal. The Giammarco-Vitro coke and the catacarb processes have improved the hot carbonate removal system by including a catalyst in the circulating scrubbing solution. The use of sulfinol solution, a mixture of diisopropylamine and sulfolane in water, can also be used to scrub the raw H for CO_2 removal.

b. Carbon Monoxide Removal—Carbon monoxide can be removed by scrubbing with a solution of cuprous ammonium acetate, or cuprous ammonium formate. Both solutions are regenerated with heat. These two systems have the disadvantages of high chemical cost, a rather complicated chemistry, requirement of very close chemical control of the scrubbing solution, and high maintenance costs.

The use of liquid N scrubbing and catalytic methanation have all but replaced copper liquor scrubbing. Liquid N scrubbing removes both CO and CH_4, and this followed by methanation gives the purest H_2 for NH_3 synthesis. Catalytic methanation employs a nickel catalyst at about 315° C to give the following reactions:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O.$$

4. Gas Compression—Synthesis

Gas reforming and purification processes operate at 0.1 to 3.4 MPa [20 to 500 pounds/inch^2 gauge (psig)]. Compression of the process gases up to eventual synthesis pressure of 13.6 to 38.4 MPa (2000 to 5000 psig) may take place at any point in the process; however, most purification processes are operated at ≤ 13.6 MPa (2000 psig) and there is a final compression

step between purification and synthesis. Most modern plants employ centrifugal compressors and the synthesis loops operate at 13.6 to 24.2 MPa (2000 to 3500 psig). Some new low-tonnage plants still employ reciprocating compressors and operate at pressures of 101 MPa (15 000 psig).

The catalytic reaction of H and N to form NH_3 is exothermic and it is favored by high pressure because there is a decrease in volume as the reaction takes place. The conversion of the reactants to NH_3 will vary from 10 to 30% for each pass of the synthesis gas mixture over the catalyst bed. In the generally used process, the purified synthesis makeup gas is compressed and added to the recycle gas within the synthesis loop. The mixed gases then pass through the water and refrigerant-cooled exchangers in the loop where the NH_3 formed in the last pass through the catalyst bed is condensed. This condensed liquid NH_3 scrubs the fresh makeup gas and removes the last traces of water and CO_2. The recycle gas, essentially free of all oxygen-containing compounds, is then reheated by exchange with the hot gas from the converter and flows to the catalyst bed in the converter at about 275 to 300°C. The reduced iron catalyst is normally contained in a vertical vessel in one or more distinct catalyst beds. The reaction is exothermic and temperatures at the exit of the catalyst beds range from 500 to 540°C. Circulation of synthesis gas through the catalyst bed normally runs from 5 to 10 times the volume of fresh makeup. Internal heat exchangers in the converters are used to control catalyst temperatures by transferring the heat of reaction to the incoming recycle gas. Some converters also add fresh makeup or quench at various points within the catalyst bed to control the bed temperatures.

Leaving the converter, the hot gas is cooled by water or by exchange with gas going back to the converter. It is then mixed with fresh makeup gases, compressed, and recycled back to the refrigeration exchangers, product separator, and converter.

Ammonia synthesis catalyst when charged consists of magnetite (Fe_3O_4) usually promoted with alumina, KCl, and Ca. The catalyst comes in the form of crushed granules nominally sized from 3 to 12 mm. Converters had a capacity of 50 to 100 metric tons/d of production about 30 yr ago, whereas today's modern plants can have converters with capacities up to 750 metric tons/d and higher.

Gases other than H_2 and N_2 are nonreacting and will concentrate in the recycle gas. These gases are unreacted methane, methane formed in the methanator, rare atmospheric gases admitted with the air injected into the secondary reformer, and H and other inert gases present in the feed gas. These must be continuously purged from the synthesis loop.

5. Ammonia by Gasification of Coal

The rapidly escalating cost of natural gas and petroleum derivatives as feedstocks for H used in production of NH_3 has focused interest on coal, a more abundant resource in the USA and other countries. The basic coal gasification technology was developed and used in Germany during World War II. South Africa has about 30 yr of further experience, and India has

two large ammonia plants based on coal. Tennessee Valley Authority was operating a demonstration plant gasifier and purification system retrofitted to an existing ammonia plant in 1983.

Investment for a coal-based ammonia plant was estimated at more than double that for a plant based on natural gas in 1982. Natural gas prices by 1990–1995 may become high enough to make the more complex and difficult coal gasification technology cost competitive.

B. Ammonia Derivatives

Anhydrous NH_3, a liquefied gas, is the most concentrated N fertilizer (82% N) available and is the raw material for all other synthetic N fertilizers. Special storage, transportation, and application equipment are required. The advantages of storing, transporting, and applying solid fertilizers and nonpressure solutions containing N have brought about the development of numerous solid- or dry-type fertilizers. With NH_3 and by-products produced by an ammonia plant, it is possible to manufacture ammonium nitrate (NH_4NO_3) and urea without additional raw materials. Other N-base fertilizers may be manufactured with NH_3 and various other raw materials. (See Table 7–1 for physical properties of these).

1. Nitric Acid

Nitric acid (HNO_3), as such, finds limited use in the mixed fertilizer industry or for agricultural purposes. But nitric acid, which is made from NH_3 and air, is reacted with additional NH_3 to manufacture ammonium nitrate.

Nitric acid is produced by oxidizing NH_3 with air at a temperature near 950° C in the presence of a platinum catalyst. The resultant gas is absorbed in water to form nitric acid. The chemical reactions for NH_3 oxidation and absorption steps are:

Oxidation	1. $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
	2. $2NO + O_2 \longrightarrow 2NO_2$
Absorption	3. $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$
	4. $2NO + O_2 \longrightarrow 2NO_2$
	5. Reactions 3 and 4 repeat through absorber

There are three types of nitric acid plants: (i) oxidation and absorption at atmospheric pressure, (ii) oxidation at atmospheric pressure followed by compression of the oxidation product gases and absorption under pressure, and (iii) oxidation and absorption under pressure.

The oxidation catalyst used in all three types of plants is Pt alloyed with 5 to 10% of Pd or Rh or both. This alloy is drawn into wire about 0.076 cm in diam and then woven into a mesh with approximately 120 openings per centimeter. The usual catalyst charge is 62 g (2 Troy ounces)/metric ton per day of 100% acid manufacturing capacity.

Table 7-1. Physical properties of solid nitrogen fertilizers.†

Fertilizer material	Formula	Molecular weight	Density	Melting point	Boiling point	Solubility in water			
						Cold		Hot	
				°C		g/kg	°C	g/kg	°C
Ammonium chloride	NH_4Cl	53	1.53	340 D	520 S	2.97	0	7.58	100
Ammonium nitrate	NH_4NO_3	80	1.73	170	210	11.83	0	87.1	100
Ammonium sulfate	$(NH_4)_2SO_4$	132	1.77	235 D	-	7.06	0	10.38	100
Calcium cyanamide	$CaCN_2$	80	-	1300 S	-	D		D	
Calcium nitrate	$Ca(NO_3)_2$	164	2.50	561	-	10.2	0	36.4	100
Oxamide	$NH_2(CO)_2NH_2$	88	1.67	256 S	290 D	0.004	7.5	-	
Sodium nitrate	$NaNO_3$	85	2.26	307	380 D	7.3	0	18.0	100
Thiourea	NH_2CSNH_2	76	1.41	180	D	0.98	12	-	
Urea	NH_2CONH_2	60	1.33	133	D	7.8	5	-	

† D = decomposes; S = sublimes.

a. Oxidation—Because pressure oxidation and absorption is the most commonly used process today, this is the process that will be described. Ammonia is vaporized and superheated to about 120° C. The superheated NH_3 vapor is mixed with hot, filtered, compressed air to give a mixture about 10.5% NH_3, by volume. This mixed gas is then preheated to about 230° C and allowed to flow over the sandwich of wire meshes that constitute the catalyst. Once lighted with either an electric filament heater or a hydrogen torch, the reaction between NH_3 and the oxygen in air is exothermic and selfsustaining. Approximately 95% of the NH_3 is converted to N oxides. The hot gases from the catalyst flow through a heat exchanger train and the heat is used for the following: (i) generate steam, (ii) preheat air, (iii) preheat air–ammonia mix, (iv) preheat tail gas from absorber, (v) preheat boiler feed water, and (vi) filter for Pt metal recovery.

b. Absorption—Processed gas from the end of the heat exchange train flows to a water-cooled dilute acid condenser. Water formed in reaction 1 is condensed here as dilute acid at 20 to 23% by weight. This dilute acid is fed to the absorber trays that operate at this acid strength. Nitric acid absorbers usually have between 30 to 35 trays with cooling of the liquid on the trays. Cooling with water is necessary because reactions 3 and 4 are exothermic and it is necessary to remove this reaction heat in order that both reactions will alternately proceed to completion to get maximum conversion of NO to NO_2 and absorption of NO_2 to make nitric acid. When properly sized and designed, an acid absorber can give about 97 to 98% efficiency.

Catalytic combustors are now included as a part of almost every new nitric process. The kinetics of reactions 3 and 4 make it impossible to convert and recover all of the N oxides. About 0.2 to 0.4% N oxides by volume will be present in the absorber tail gas. This gas, which contains 2 to 3% oxygen by volume, is reheated, mixed with a hydrogen or hydrocarbon fuel, and is then passed over the catalytic combustor catalyst. Active catalysts can reduce most of the N oxides to N. This reaction is also exothermic and thus will increase the tail gas temperature for additional power recovery when let down through a hot gas expander.

2. Ammonium Nitrate

Ammonium nitrate (NH_4NO_3) is a logical solid fertilizer for manufacture in a synthetic ammonia plant. Nitric acid is manufactured, which, in turn, is neutralized with additional NH_3 to form ammonium nitrate. Ammonium nitrate is a white crystalline solid containing 350 g N/kg (35% N). (The fertilizer grade material after coating with a conditioning agent contains 33.5 to 34.0% N). About 75% of the ammonium nitrate produced is used to manufacture dynamite, high explosives, and solid rocket propellants; it can be mixed with about 6% fuel oil by weight as a substitute for dynamite.

The reaction between ammonia and nitric acid to produce ammonium nitrate is a simple acid-base neutralization reaction:

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3.$$

Vaporized and superheated ammonia and nitric acid are sparged or injected below the liquid level in the neutralizer. The reaction is exothermic and the heat of reaction is sufficient to concentrate the neutralized solution to about 83%. It is then further concentrated to 95 to 96% and pumped to the top of a prilling tower. From here it is sprayed and, in falling to the bottom of the tower through a counter-current air stream, the drops of solution chill and solidify. The solid prills are collected at the bottom of the tower, screened to remove oversized material, and then conveyed to one or more dryers where heated air is employed to reduce the moisture content to $\leq 0.5\%$. The dried prills are cooled and again screened to remove over- and undersized material. The dry, cooled ammonium nitrate is then coated with about 3% clay or parting agent to minimize moisture pickup from the atmosphere, prevent caking, and keep the product free-flowing.

An alternate to this process is the use of a shorter tower and the prilling of an ammonium nitrate melt at a concentration of about 99.8%. The solid prills will contain $\leq 0.2\%$ moisture; therefore, it requires no additional drying. Prills produced by this process are slightly more dense than prills made from prilling a 95 to 96% solution.

The Stengel process also produces a high-density ammonium nitrate, but the product is angular as opposed to the smooth, round prill produced by the prilling process. Nitric acid is preheated in this process to further increase the reaction heat and water vaporization from the neutralizer. Ammonium nitrate solution from the neutralizer is concentrated to a melt of near 99.8% and is flowed onto a cooled continuous stainless steel belt. The melt solidifies on this belt and is then chipped off, ground, and screened to give the desired particle size. The product is cooled and coated with clay.

Ammonium nitrate for fertilizer use is also produced in granular form by *spray-drum* granulation (spherodizing) and by granulation in revolving inclined pans. (Reed & Reynolds, 1973; TVA, 1980). The granules are harder and more durable and can readily be produced in larger size.

Ammonium nitrate in all its forms is a strong oxidizer, but it is not an explosive in its pure form or when mixed with other major nutrients. Before mixing with metals or carbonaceous materials, safety precautions should be observed.

3. Ammonium Sulfate

Most of the ammonia used in agricultural ammonium sulfate [$(NH_4)_2SO_4$] is produced as a by-product of coal coke ovens and in caprolactum manufacture; however, it may also be made synthetically. The reaction is the same for both sources of NH_3

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4.$$

Ammonium sulfate is a white crystalline solid, slightly less soluble in water than urea, with a N content of 21%. It is an excellent source of the secondary nutrient S. The shift to higher-analysis fertilizers, such as ammonium nitrate and urea, has reduced the ammonium sulfate market to the point that by-product ammonium sulfate alone will satisfy the demand. By-product ammonium sulfate generally enjoys a cost advantage over the synthetic product; by virtue of this and the oversupply situation, there is very little synthetic material being produced in the USA today.

The process takes place in a reactor or saturator where sulfuric acid (H_2SO_4) and superheated NH_3 gas are sparged into a supersaturated solution of ammonium sulfate. The reaction is exothermic and water is added to vaporize as steam and thus dissipate the heat of reaction. The crystals that form are maintained in suspension by agitation or forced circulation. The crystal growth and size can be controlled by the length of time the crystal remains in the saturator, by reactor temperature, by the percent free acid in the saturator, and by the liquor recycle rate. When crystals reach the desired size, a continuous drawoff of solution and suspended crystals is started. This drawoff stream is filtered or centrifuged to recover the crystals, and the filtrate (mother liquor) is returned to the saturator. The crystals are then dried with heated air, cooled, and coated.

4. Urea and Urea Derivatives

a. Urea—Like ammonium nitrate, urea is a well-integrated product for a synthetic ammonia plant (Scaglione, 1963; Anon., 1963). The two feed streams required for the manufacture of urea are ammonia and carbon dioxide, both of which are products or by-products of an ammonia plant. The general reaction for producing urea is:

$$CO_2 + 2NH_3 \longrightarrow CO(NH_2)_2 + H_2O$$

Urea is a white crystalline solid, very soluble in water, and the clay-coated agricultural grade is 45% N.

There are many variations of urea manufacturing processes; most of the variations are in the methods used to recover, separate, and recycle unreacted NH_3 and CO_2. The various processes may also be subdivided into: once-through, partial recycle, and total recycle.

The urea reactor is a large continuous autoclave in which compressed CO_2 gas and heated liquid NH_3 are reacted at 19.2 to 27.3 MPa (2800 to 4000 psig) and 180 to 195° C. The reactants combine to form urea and ammonium carbonate [$(NH_4)_2CO_3$]. Conversion and eventual recovery of ammonia N as urea N will run about 30% for the once-through process, 50 to 80% for the partial recycle processes, and up to 98% for the total recycle process. Most processes, if not all, operate with excess NH_3 in the reactor. The solution from the reactor is heated to dehydrate the carbonate to form urea and water, and then the different methods of separating, recovering, and recycling the unreacted NH_3 and CO_2 and the carbonate that is not decomposed come into use. These are so numerous and complicated that no attempt will be made to discuss them in this book.

Either prills, granules, or crystals may be produced for the end product. Urea solution from the reactor at 75 to 87% concentration is vacuum-concentrated to 99.7% melt that is either prilled or granulated (Reed & Reynolds, 1973; TVA, 1980, 1982). For some uses, the urea is first crystallized and then melted and prilled or granulated. An additive in small proportion provides good storage and handling properties without a surface coating. Grade of product urea is 46% N.

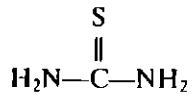
Urea became the world's leading N fertilizer in the mid-1970s.

b. Sulfur-Coated Urea (SCU)—Granular or prilled urea may be coated with S and a sealant to give a controlled-release N fertilizer (TVA, 1966, 1968, 1979). The solid urea is preheated to 65 to 70° C and molten S at 143° C is then atomized and sprayed onto the urea in a rotary drum. This is followed by a spray of the molten wax-like sealant (polyethylene-brightstock mixture). The urea is preheated so that the molten S does not chill too quickly and gives a uniform coating. The material is then cooled and coated with a conditioner. Typical finished product contains 36% N and analyzes about 78% urea, 17% S, 2% sealant, and 2.5% diatomaceous earth conditioner.

c. Urea-Formaldehyde—Urea-formaldehyde or ureaform also is a slow-release N fertilizer, but unlike SCU, it is slowly water soluble. Ureaform is a slightly hygroscopic, odorless, white, granular solid containing about 38% N. Actually, the term *ureaform* covers many products that are mixtures of methylene ureas. They range from short-chain water-soluble molecules to long-chain water-insoluble molecules.

Ureaform encompasses urea-formaldehyde products from the urea-formaldehyde resins or plastics with almost completely unavailable N to products with some unreacted urea along with methylene ureas, which give both readily available and slowly available N.

d. Thiourea—Thiourea is a crystalline, colorless solid (prisms or needles) having the formula



and a melting point of 180 to 182° C. It is relatively insoluble in water and only slightly soluble in ether. The three most common methods of preparation are (i) heating ammonium thiocyanate (NH_4CNS) to about 180° C, where equilibrium with thiourea is established; (ii) the reaction of hydrogen sulfide at about 180° C with calcium cyanamide; and (iii) the reaction of dicyandiamide and ammonium sulfide at 60 to 70° C.

e. Crotonylidene Diurea—Crotonylidene diurea is currently used in nonfarm applications as a slow-release N fertilizer. It is a high-cost product manufactured by the reaction between cronotonaldehyde and urea. The chemical name for this material is 2-oxo-4-methyl-6-ureidohexahydropyrimide.

f. New Urea Forms—Other urea fertilizers in the slow-release group are being investigated for their advantages in economics and manufacture and for their agronomic value. Some examples of these are propylidene diurea, isobutylidene diurea, trifurfurylidene triurea, and urea pyrolzates. Information on the soil reactions of the slow-release materials is included in another chapter.

5. Other Ammonium Fertilizers

a. Ammonium Nitrate–Sulfate—This material, which is manufactured by at least one major fertilizer supplier, is produced by granulating ammonium nitrate onto ammonium sulfate nuclei and then coating the finished product with a conditioning agent. It can also be manufactured as a double salt of ammonium sulfate and ammonium nitrate containing 26% N. Its main use is to provide nutrient S that is needed in some areas and cropping situations.

b. Ammonium Chloride—Fertilizer-grade ammonium chloride (NH_4Cl) is generally recovered as a by-product from an ammonium soda operation or Solvay Process plant. In the Solvay Process, a brine solution is ammoniated and then carbonated; sodium bicarbonate and ammonium chloride are formed and the solution still contains considerable unreacted sodium chloride. The sodium bicarbonate, sparingly soluble in this mixture of salts, is separated from the liquor by filtration and then converted to soda ash by heating.

C. Other Nitrogen Fertilizers

1. Calcium Nitrate

Calcium nitrate [$Ca(NO_3)_2$] is manufactured principally in Europe as a coproduct of nitric phosphate production. It is a white crystalline hygroscopic solid containing 15.5% N. It can be produced by reacting nitric acid and crushed limestone as shown in the following equation:

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + CO_2 + H_2O.$$

The co-product calcium nitrate from nitric phosphate production is coated with paraffin as a conditioner for the hygroscopic material. Calcium nitrate is popular in Europe but is not widely used in the USA, because of its low N content and the availability of lime-nitrate-urea fertilizers. Its principal use in the USA is on citrus, for which it is well suited.

2. Sodium Nitrate

Essentially all sodium nitrate ($NaNO_3$) used for fertilizer purposes is a natural product mined and processed in Chile. However, a synthetic sodium-nitrate process has been used in the USA. In this process, salt and a 70% HNO_3 are heated to boiling in a reaction vessel, evolving chlorine and nitrosyl chlorine as shown in the reaction below:

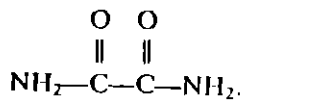
$$3NaCl + 4HNO_3 \longrightarrow 3NaNO_3 + Cl_2 + NOCl + H_2O.$$

The evolved gases are then oxidized with hot 80% HNO_3 in a column to produce nitrogen dioxide and chlorine, as indicated by the following reaction:

$$2NOCl + 4HNO_3 \longrightarrow 6NO_2 + 2H_2O + 2Cl.$$

3. Oxamide

Oxamide is a slow-release N fertilizer that in pure form has a N content of 31.8%. It has the structural chemical formula



Recent work on the production of oxamide has been conducted in the USA (TVA), Federal Republic of Germany (Hoechst A. G.), and Japan (Ube Industries). Hoechst has developed a process to pilot-plant stage in which hydrogen cyanide is oxidized in an acetic acid/water mixture with a copper nitrate catalyst (Riemenschneider, 1976). TVA's laboratory studies have centered around the oxidative carbonylation of alcohols with palladium catalysts and quinone oxidants in a single-step process. Ube Industries' work has been similar to TVA's but in a two-step operation.

The slow-release characteristics of oxamide depend to a large extent on its granule size. Some evidence also indicates that certain bacterial action is required before N is released. Cost of production is projected as substantially higher than for N as urea, and for that reason the use of oxamide would be restricted to specialty fertilizer markets.

4. Calcium Cyanamide

One of the oldest methods employed for the fixation of atmospheric N for agricultural purposes is the nitrification of calcium carbide to form calcium cyanamide ($CaCN_2$). The first step in this process is the production of calcium carbide by fusion of lime and coke. This is carried out in an electric arc furnace to provide the high level of temperature needed. The following reaction occurs:

$$CaO + 3C \longrightarrow CaC_2 + CO$$
$$CaC_2 + N_2 \longrightarrow CaCN_2 + C.$$

The second step of the process is initiated at approximately 1000° C and, once started, is self-sustaining.

Pure N must be used to avoid oxidizing the carbide to lime and carbon monoxide. These operations must be blanketed in an inert atmosphere to avoid explosions.

Calcium cyanamide is only produced in Europe. Total production was < 55 000 metric tons of N in 1980.

D. Solutions Containing Nitrogen

Liquid anhydrous NH_3 is by far the leading form of N fertilizer applied in the USA. Table 7–2 shows N consumption by types of fertilizer in 1982.

Water solutions of any solid N fertilizer may be used for direct application or as the N source for blended or granulated fertilizers. Ammonia, ammonium nitrate, and urea are the most commonly used N compounds in fertilizer solutions.

1. Aqua Ammonia

Water solutions of NH_3 are commonly referred to as *aqua* and the most widely used concentration is about 25% NH_3, which corresponds to 20% N. Some aqua is made at the ammonia plant and shipped to the consumer, but the preferred procedure is to ship anhydrous NH_3 to the retail point where it is then converted to aqua. Manufacture in the field is accomplished by metering and mixing the NH_3 and water, followed by cooling to remove the heat of mixing. The reaction or mixing heat is quite high, and the product must be cooled to a temperature of about 32° C to bring the total vapor pressure down below the atmospheric pressure and thus minimize NH_3 loss from the solution.

2. Ammonium Nitrate

Ammonium nitrate–water solutions are used almost exclusively for blending mixed fertilizer solutions and as the N source for granulated fertilizer. The most commonly used solution contains 83% ammonium nitrate, which has a crystallization temperature of 66° C and a density of 1.385.

3. Ammonium Nitrate–Urea–Ammonia

The main constituents used in ammonium nitrate–urea–ammonia solutions are ammonium nitrate and urea with ammonia added in some types. Different combinations of these ingredients are used to obtain the desired properties. These solutions may be classified into two types—low pressure and nonpressure.

Table 7–2. Consumption of various types of N fertilizers in 1982.

Fertilizer type	Application
	metric tons of N × 10^6
Anhydrous NH_3	4.7
Nitrogen solutions	2.3
Solid urea	1.1
Solid ammonium nitrate	1.0
Ammonium sulfate	0.16
Aqua NH_3	0.14

The low-pressure solutions contain free NH_3 and are used primarily for ammoniating superphosphate. These solutions have a wide range of vapor pressure [0.07 to 3 MPa (1 to 50 psig) at 40° C] and crystallization temperature (−45 to + 10° C). Nitrogen analysis varies from 37 to 49% N. For direct application, these solutions have the advantage of lower vapor pressures than anhydrous NH_3 and higher N analyses than aqua.

4. Urea–Ammonium Nitrate Solution

The nonpressure urea–ammonium nitrate solutions contain ammonium nitrate and urea. The high mutual solubility of the two salts gives a relatively high-analysis solution containing 32% N and makes it one of the most popular of the N solutions. This solution normally contains 33 to 35% urea, 45 to 47% ammonium nitrate, and 32% N. The solution has a density of 1.33 kg/L and a crystallization (salting-out) temperature of 0° C. The addition of sufficient water to dilute this solution to 28% N gives a solution with a density of 1.285 kg/L and a crystallization temperature of −18° C.

5. Others

There are also a few special solutions that are used to supply the supplemental elements—Na, Ca, or S solutions—when necessary for special soil or crop requirements. These include sodium nitrate–ammonium nitrate (20% N), calcium nitrate–ammonium nitrate (17% N), ammonium bisulfite (8.5% N, 19.4% S), and ammonium polysulfide (20.6% N, 45% S).

E. Mixed Fertilizers Containing Nitrogen

Mixed fertilizers are important to agriculture but are difficult to cover. Only introductory treatise is given in this chapter with more detailed information in chapters 9, 10, 12, and 13 of this book.

1. Potassium Nitrate, 13.85–0–38.66 (13.85–0–46.39)

In a pure state, potassium nitrate (KNO_3) contains 13.85% N and 38.66% K. It is also known as salt-peter or nitre and is a white, crystalline solid. It has been produced domestically for years by the double decomposition reaction between sodium nitrate and potassium chloride (KCl), which follows:

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl.$$

In this process, solid potassium chloride is reacted in a hot solution of sodium nitrate. Sodium chloride is crystallized from solution and is separated from the hot potassium nitrate liquor. Solid potassium nitrate is produced by subsequent crystallization and filtration. More information on this product is given to chapter 10 of this book.

2. Urea-Phosphate, 17.7–19.6–0 (17.7–44.88–0)

Urea-phosphate is an additional compound of urea, a very weak base, and phosphoric acid (H_3PO_4), a relatively strong acid. A white, crystalline, dry powder is formed, which contains 17.7% total N and 19.6% P. Its specific gravity is 1.759 and its melting point is 117.5° C. This product, known as carbamide–phosphoric acid, is very soluble in water (202 g/L at 46° C).

Urea-phosphate is prepared by the reaction of concentrated phosphoric acid and solid urea:

$$CO(NH_2)_2 + H_3PO_4 \longrightarrow CO(NH_2)_2\,H_3PO_4.$$

The product is precipitated by cooling and recovered by filtration.

TVA is conducting pilot-plant studies of the production of urea phosphate from wet-process phosphoric acid and urea. In one process, the urea phosphate crystals are separated by centrifuging as comparatively pure material containing 17% N and 19% P (17–19.36–0) (17–44–0). Only about 15% of the impurities from the wet-process acid are retained in the product. That is a good intermediate for preparation of liquid fertilizers of high quality. The urea phosphate crystals are agglomerated by heat of fusion in a simple system to give the product good handling and shipping properties.

In an alternative process, the reaction mass of urea and wet-process acid is granulated in a specially designed drum reactor–granulator. The product granules contain 16% N and 18% P (16–41–0) (16–18.04–0). The product made by the simpler and lower-cost process contains all of the impurities from the acid, so it would not be suitable for production of liquid fertilizers of low-impurity content. It loses very little N on surface application and shows good promise in decreasing the loss of N from mixtures with urea.

3. Ammonium Phosphates

The term *ammonium phosphates* encompasses a wide variety of fertilizers produced by ammoniation of phosphoric acid. Such fertilizers may contain ammonium sulfate or ammonium nitrate as an additional source of N; the ammonium phosphate may be present as the monoammonium or the diammonium salt or mixtures of the two. More detailed information is presented in chapter 9 of this book.

4. Other Ammonium Phosphates

a. Metal Ammonium Phosphates—Small-scale production of a number of metal ammonium phosphates having the general formula

$$MeNH_4PO_4 \cdot XH_2O$$

have been produced on a pilot-plant basis. These compounds are capable of supplying N, P, and various metals over long periods of time. A magnesium ammonium phosphate containing 8% N, 17.5% P, and 14.5% Mg is an example of these compounds.

b. Ammonium Polyphosphates—Ammonium polyphosphate fertilizers are made by reacting ammonia and superphosphoric acid. In the process, the acid and ammonia are reacted at moderate pressure and at an elevated temperature to produce a fluid melt, which is granulated. This solid product contains about half monoammonium phosphate and half ammonium polyphosphate.

Ammonium polyphosphate can also be produced by ammoniation of orthophosphoric acid, using the heat of reaction to evaporate water and form polyphosphate. This process, utilizing merchant-grade wet-process acid, is currently in operation. For more details see chapter 9 of this book.

Superphosphate, monoammonium phosphate (MAP), or diammonium phosphate (DAP) are used as sources of phosphate to make suspension fertilizers that are less costly than ammonium polyphosphate. A small amount of clay is added to promote suspension of the fine solid nutrients. Suspensions allow higher-analysis triple nutrient fertilizers than liquids (solutions), plus the addition of higher concentrations of secondary and micronutrients, herbicides, and insecticides with manageable physical properties. See chapter 12 of this book for more details.

III. ENERGY REQUIREMENTS

A. Energy for Fertilizer Manufacturing

For comparative purposes, average energy requirements for manufacturing common nitrogen, phosphate, and potash fertilizers are summarized in Table 7–3. These estimates are based on an energy-use survey in North America during 1979 and information from other sources. Consequently, these estimates are representative of actual energy use by fertilizer plants in operation. However, one must be careful in generalizing these estimates for the developing countries because of the differences in technology, processes, management, and efficiency. As a result, the energy requirements in manufacturing fertilizers may be underestimated for developing countries. Furthermore, the energy requirements are based on high heating value and total rather than battery-limits energy estimates.

There is a substantial variation in energy requirements across different fertilizers, ranging from 79.5 GJ/metric ton of nutrient content for prilled urea (highest) to 3.8 GJ/metric ton for nongranular potassium chloride (among the lowest). Both phosphate and potash fertilizers use very little energy; most of it is in the form of fuel, electricity, and steam. Since steam and electricity can be generated from any commercial fuel, the manufacture of phosphate and potash fertilizers presents a fairly wide latitude in choice of basic energy sources. On the other hand, N fertilizers are highly energy-intensive and require energy both as feedstock (source of H for NH_3) and fuel (including steam). Most of the direct and indirect energy uses in the existing fertilizer sector depend primarily on nonrenewable hydrocarbons.

Table 7-3. Average energy use for manufacturing selected nitrogen, phosphate, and potash fertilizers.

Product	Percent nutrients	Average energy input, GJ	
		Per metric ton of product	Per metric ton of nutrient
Nitrogen fertilizers (N)			
Ammonia	82	46.9	57.2
Urea: prilled	46	36.6	79.5
granular	46	35.0	76.1
Ammonium nitrate: prilled	34	24.9	73.4
granular	34	24.4	71.8
Ammonium sulfate: synthetic	21	12.6	60.6
by-product	21	4.7	22.4
Phosphate fertilizers (P)†			
Ground rock‡	13	1.2	9.2
Phosphoric acid	24	5.3	22.1
TSP, granular	20	4.3	21.5
DAP, granular	20	14.3§	20.0
MAP, granular	24	10.8¶	16.8
SSP, nongranular	9	1.0	11.1
SSP, granular	9	1.7	18.9
Potash fertilizers (K)			
Muriate:# granular	50	2.9	5.8
nongranular	50	2.3	4.6
average	50	2.6	5.2
Muriate:†† average	50	4.6	9.2

† TSP = triple superphosphate; DAP = diammonium phosphate; MAP = monoammonium phosphate; SSP = single superphosphate.
‡ For direct application, dried, and finely ground.
§ Contains 18% N. Energy use is 57.2 GJ/metric ton of N.
¶ Contains 11% N. Energy use is 57.2 GJ/metric ton of N.
# For North America.
†† For Europe.

The production of urea requires commercial energy, which is over 8 times that of triple superphosphate (TSP) and 19 times that of potassium chloride. This is precisely the reason why many countries that produce NH_3 based on imported feedstocks find it difficult to continue operating the existing N fertilizer industry or plan to phase it out.

B. Energy For Fertilizer Distribution

After the chemical fertilizer is manufactured, commercial energy is also required to pack it in bags, transport it to the farm level, and apply it to the crop. However, the total amount of energy required for fertilizer distribution and application is rather small relative to its manufacture. The major share of energy required for distribution is used in transportation of fertilizer products and raw materials.

Average energy use for fertilizer packaging, transportation, and application is 8.6 GJ/metric ton of N, 22.4 GJ/metric ton of P, and 8.8 GJ/metric ton of K. Of this amount, transportation accounts for 52, 58, and

63%; packaging accounts for 30, 27, and 24% for N, P, and K, respectively. In the case of P and K, since their manufacture is relatively less energy-intensive, packaging and transportation account for approximately 46% of the total energy needs on a nutrient basis.

Even though it is difficult to make any generalizations, two other features for fertilizer transportation stand out. First, trucks are the most common mode of transporting fertilizer, especially at the secondary level. Second, truck transportation is highly energy-intensive. On the average, trucks use four times more energy than rail and almost nine times more energy than waterways for transporting 1 metric ton of fertilizer for a distance of 1.6 km.

C. Energy Conservation

Work has been intense since the early 1970s in efforts to decrease the energy required to produce ammonia, urea, and other nitrogen fertilizers. Engineering firms who design and construct process plants have developed schemes for substantial decreases in natural gas requirements for process needs and fuel in new ammonia plants. In new ammonia and urea processes, various schemes have been worked out to decrease energy requirements as electricity and steam, and to more efficiently utilize available process heat.

Some of the more effective schemes for energy conservation can be retrofitted to existing plants. Benefit/cost ratios often greatly favor the required investments.

IV. TRANSPORTATION AND MARKETING OF NITROGEN FERTILIZERS

Close to 10.6 million metric tons of actual N in fertilizer materials are transported from manufacturing plants to distribution terminals, dealer storage, and farms in the USA. This volume is increasing and has made it necessary to develop improved systems of marketing and of movement by railcars, trucks, barges, and pipelines.

A. Transportation

Railcars are the primary means of N fertilizer transportation. The economy in rates has improved by increasing the capacity of the cars from 24 to 72 metric tons. Rail rates are reduced further through multiple-car shipments.

Some of the most significant changes have been in the transport of nitrogenous fertilizers. There are now approximately 15 000 ammonia railcars in service. Twenty-four metric ton capacity railcars are used within a radius of 320 to 645 km from manufacturing plants, terminals, and other distribution points. The 72 metric ton capacity (jumbo) cars are used be-

tween distances of 645 to 1600 km with the multiple-car shipments used for the longest distances.

River barges are also used to transport 6300 to 9000 metric ton quantities of fertilizer from Gulf Coast production points to terminals in the Corn Belt. Many smaller capacity barges are now obsolete and are no longer used.

Trucks, carrying approximately 18 metric tons, transport fertilizer from 1 to 480 km to retail points and farms with more economy than any other means. One truck, because of its quick turn-around time, can transport as much fertilizer on short hauls as 25 small railcars. The N fertilizer industry in the USA is built around anhydrous NH_3, partially because of its relatively low per-unit cost. Continued competitive advantage will cause consumption to increase. Its physical characteristics, which make pipeline transportation possible, adds considerably to its efficiency and demand.

Pipelines have been built and are operating on the concept of satisfying the foregoing market conditions. The new relationship between the cost of natural gas and freight rates has made the location of production plants a major economic consideration. The majority of new ammonia plant capacity in the USA has been constructed in the gas-producing areas of Texas and the Gulf Coast.

A kind of three-ring circle of service has developed along the pipelines, with the pipeline acting as the long-distance transporter. The inner ring is small trucks of 11 500 to 19 000 L water capacity loading at pipeline terminals and distributing the load directly to farm applicators within a radius of 50 km. The second ring, from 50 to 180 km, is large truck transports with 38 000 to 42 000 L water capacity, loading at pipeline terminals and distributing the load to bulk plants having 45 000 to 67 000 L of storage. The outer ring is tank cars delivering to bulk plants having 76 000 to 227 000 L of storage and served by railroads that can provide prompt service on demand.

Pipeline terminals consist of high-pressure storage tanks and truck loading docks capable of loading 100 transports per day and are located at strategic points along the pipeline. Deliveries of anhydrous NH_3 to the terminals are regulated from a central traffic control center.

Two emergency shut-down stations, one located at the truck dock and the other at the terminal building, can be used to shut down the entire terminal in case of an emergency.

The first anhydrous NH_3 pipeline was MAPCO's 1300-km line (Mid-American Pipeline System) from production at Borger, TX, to distribution points in Kansas, Nebraska, and Iowa. Its capacity is 1170 metric tons/d. The Gulf Central Pipeline Company system is about 2700 km long and has a capacity of 1 million metric tons/yr or 2700 metric tons/d. Ammonia enters this pipeline at Luling, LA, and at Donaldsonville, LA. A 1100-km truck line leads to a junction at Herman, MO. An eastern branch goes to markets in Illinois and Indiana, and a western branch serves Iowa and eastern Nebraska (See Fig. 7–3).

Nonpressure N fertilizer solutions are increasing in usage. Railcars, barges, and trucks are transporting the bulk of this product. Moving and

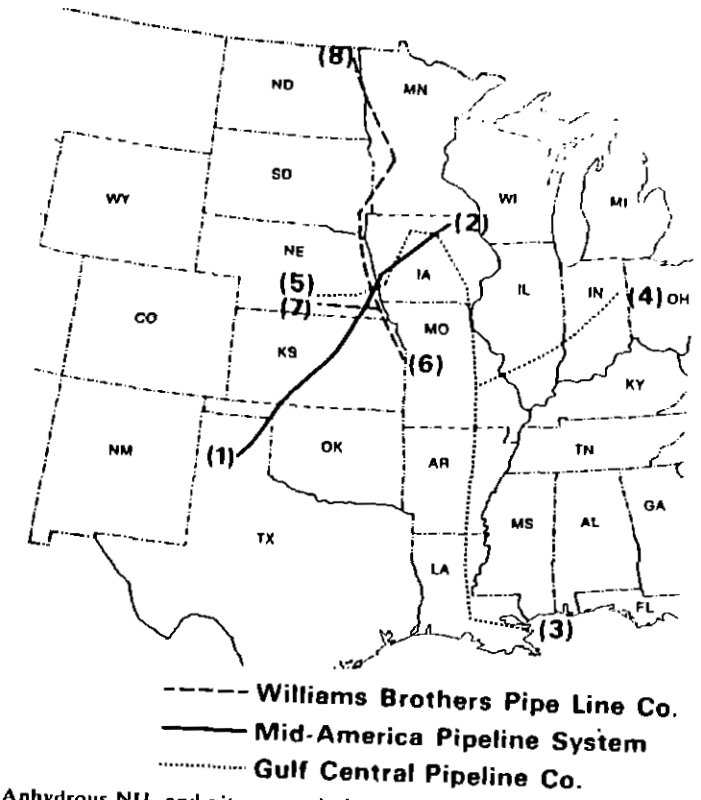


Fig. 7–3. Anhydrous NH_3 and nitrogen solution carrying pipeline. Mid-America starts at Borger (1) and ends at Gamer (2); Gulf Central starts at Luling (3) and runs to Huntington (4) or to Garner (2) and then Aurora (5); Williams Brothers begins at Kansas City (6) and proceeds to Doniphan (7) or Grand Forks (8).

distributing these materials through existing petroleum pipelines is feasible and one pipeline company (Williams Brothers Pipe Line Co., Fig. 7–3) is now moving fertilizer solutions from Kansas City to points in Nebraska, Iowa, Minnesota, and North Dakota. Even though this means of transporting solutions is in its infancy, it is expected to increase with usage of these products.

B. Marketing

Marketing N fertilizers, as we know it today, becomes a set of coordinated forces that makes things happen beyond the point of production. The old marketing concept in which

1. the *focus* was production capacity,
2. the *means* was selling and promotion, and
3. the *end* was profit through volume

has proven itself to have serious limitations. The need for change has been brought about by three factors: first, we now produce and have for sale more fertilizer than the farmers are using; second, the numbers of retailers

have increased; and third, the levels from which farmers make the decision to buy have been elevated.

The general marketing policy calls for
1. the *focus* point to be the farm customer,
2. the *means* to be integrated marketing, and
3. the *end* to be profit through customer satisfaction.

This is accomplished through more and more customer services.

Nitrogen fertilizers are marketed through efficiency-oriented channels between the manufacturer and retailer. This does not differ from the marketing of the other fertilizer products. The manufacturers are also known as suppliers and have their own sales organizations who service the retailer. Some brokers exist but are few in numbers and sell limited quantities. The two types of retail organizations are independent retail businesses and supplier-owned retail centers.

1. Independent Retailers

In the independent retailer operation, all degrees of ownership of land, storage, and handling of equipment exist. These may be owned by the retailer, but in many instances the supplier retains ownership to maintain a permanent outlet for the product.

An independent retailer may buy the product as an on-the-spot purchase or contract for resale. Some independent retailers operate as a contracted commission agent and never hold ownership of the product, and the supplier carries the accounts receivable.

Application equipment is usually owned by the retailers because of its maintenance problems.

2. Supplier-Owned Retail Centers

In the supplier-owned retail center operation, all land, storage and handling, and application equipment is owned and managed by the supplier; all personnel and management decisions are made by the supplier. The advantage of this type of outlet is that the supplier controls all aspects of the business and retains ownership of the physical plant to assure a favorable position for the future.

Agricultural colleges have been active in determining the merits of the various types of N fertilizers. They have also ascertained the best time, rates, and types of application. Most manufacturers and retailers base their sales approach and recommendations on research reports and recommendations published by their respective state universities.

V. TRANSFORMATIONS OF NITROGEN SOURCES IN SOILS

About 90% of the fertilizer N used in the USA is in the form of NH_3 or ammonium-producing compounds and about 65% of this amount is anhydrous NH_3. The remainder is chiefly accounted for by nitrate in ammonium nitrate. Improving N fertilizer effectiveness requires an understanding of the factors governing N fertilizer transformations in soils. This section will discuss the short-term chemical and biological transformations of fertilizer N in soils, as well as their long-term behavior, which considers the fate of added fertilizer N, e.g., leaching and denitrification.

A. Immediate Reactions of Mineral Nitrogen Fertilizers

The direct reactions of mineral N fertilizers center on the chemical transformations of ammonia and nitrate immediately after application, as opposed to slower transformations that take place over several days or months.

1. Transformations of Nitrate Ions

Nitrate-N (NO_3^-–N) is relatively unreactive in soils because (i) nitrate compounds are readily soluble and (ii) there is little tendency for them to be adsorbed on the negatively charged surfaces of soil colloids. Nitrate is therefore susceptible to movement through diffusion and mass transport in the soil water.

2. Transformations of Ammonia and Ammonium Ions

If ammonium salts are applied uniformly to a soil, ammonium ions can undergo cation exchange reactions and/or precipitation of insoluble reaction products [e.g., calcium sulfate ($CaSO_4$) from ammonium sulfate]. Since ammonium-N (NH_4^+-N) is held by the negatively charged soil colloids, there is little tendency for it to move with the soil water in most agricultural soils, which have cation exchange capacities (CEC) > 2.

If ammonium fertilizers are applied to a localized zone, however, the area around the application zone becomes dominated by the chemistry of the N source. The scale of this fertilizer-dominated zone may be large (e.g., the 5-cm diam zone around an anhydrous NH_3 injection) or small (e.g., the 5-mm zone around a urea granule) depending on factors such as soil texture, pH, organic matter content, water content, and N source. Initial effects of acidic N sources (ammonium nitrate, ammonium sulfate, monoammonium phosphate) involve mainly cation exchange reactions and precipitation reactions. Initial reactions of basic N sources (anhydrous NH_3, urea, diammonium phosphate) are more complex and include (i) the hydrolysis of urea to ammonium carbonate, (ii) a rise in pH, often to ≥ 9.0, (iii) a very high level of NH_3 and NH_4^+, often > 2000 mg/kg, and (iv) a decline in the number of soil organisms, including nitrifying organisms (Frederick & Broadbent, 1966; Pang et al., 1973; Wetselaar et al., 1972; Creamer & Fox, 1980; Hauck & Stephenson, 1965). The initial sink for NH_3 is the soil solution, because NH_3 is very soluble in water (42 g NH_3–N/100 g of water at 20° C) (Sharp, 1966). The distribution between NH_3 and NH_4^+ is determined by the pH (Fig. 7–4) according to the equation:

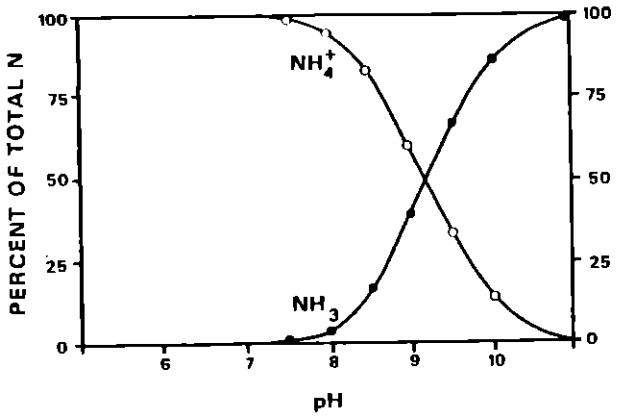


Fig. 7–4. Percent of total N as NH_3 and NH_4^+ at various pH levels.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O. \qquad [1]$$

Dissolved NH_3 will move in response to diffusion gradients and mass flow of the soil solution. It will be converted to NH_4^+ by reacting with water, clay minerals, and organic matter. Soil inorganic fractions supply hydrogen ions (H^+) for this conversion from exchangeable H^+ on the exchange complex, from hydroxyl groups on the edge of clay minerals, and from the dissociation of water on clay-adsorbed hydrated ions such as aluminum (Al^{3+}) or calcium (Ca^{2+}) (Mortland, 1966). The soil organic fractions supplies H^+ from carboxyl groups (–COOH) and phenolic groups (–OH) (Broadbent & Stevenson, 1966). It is important to note that soils have a large capacity to absorb NH_3 over a broad pH range. The soil CEC is a dominant factor in such retention because it is related to clay content, type of clay, and organic matter content. Under acid conditions, NH_3 retention is probably dominated by reactions with soil minerals; retention under basic conditions is primarily associated with the organic fraction (Parr & Papendick, 1966).

3. Ammonia Fixation in Organic and Mineral Forms

By and large, the above NH_3 transformations produce NH_4^+, which is chemically and physically accessible for plant uptake. Other direct reactions can occur, however, which place the fertilizer N in compounds of low biological availability.

Some of the NH_3 may be chemically fixed by reacting with organic matter. The reaction mechanisms are vague, but are thought to involve NH_3 reacting with oxidized lignin and various quinones accompanied by polimerization, which results in complexes resistant to dissolution and enzyme action (Broadbent & Stevenson, 1966). These chemical fixation reactions are favored by high pH and high NH_3 concentrations; these are the expected conditions in an anhydrous NH_3 injection zone.

The ion NH_4^+ is also subject to chemical fixation within the crystal lattice of expanding 2:1 clay minerals (e.g., vermiculite, illite). It is just the right size to enter into the hexagonal openings between oxygen atoms of the silicon layer of clay minerals. If the crystal lattice contracts, NH_4^+ becomes fixed and is not readily accessible for ion exchange reactions. Potassium interacts with NH_4^+ fixation and release because it is the same size as NH_4^+. Potassium can maintain a clay lattice in a contracted state and thus block the release of fixed NH_4^+. A soil's capacity to fix NH_4^+ increases with its content of expanding 2:1 clays, with pH, and with the NH_4^+ concentration. These conditions will most readily occur in an alkaline high NH_3 environment. The biological availability of fixed NH_4^+ has generally been considered to be small, based on many laboratory and greenhouse studies (e.g., Mortland, 1966). Fixed NH_4^+ is not readily nitrified, but it may be slowly released over the course of a growing season depending on the K status of the soil. Recent field investigations show fixed NH_4^+ to be more readily available to crops than was previously thought, possibly because the plant is removing interfering K^+ (Nommik, 1981; Kowalenko, 1978; Kowalenko & Cameron, 1978; Van Praag et al., 1980).

B. Nitrification of Ammonium Fertilizers and Other Biological Interactions

Nitrification of ammonium salts was investigated for a number of years before anhydrous NH_3 and urea came into prominence. These studies revealed the nature of nitrification and the importance of environmental factors such as soil pH, soil water content, aeration, and temperature (Allison, 1973; Black, 1968). In general, the conversion of NH_4^+ to NO_3^- seldom affects plant growth, particularly if the NH_4^+ is dispersed throughout a large volume of soil. However, the practice of NH_3 injection and localized urea application has imposed a new set of conditions on the nitrification process.

Nitrification is the biological oxidation of NH_4^+ to NO_3^-, which can be represented by the following equation:

$$NH_4^+ \xrightarrow[+\ \text{oxygen}]{\textit{Nitrosomonas}} H^+ + NO_2^- \xrightarrow[+\ \text{oxygen}]{\textit{Nitrobacter}} NO_3^-. \qquad [2]$$

Three important features of nitrification are apparent (i) it is a biological process, which means it is affected by several environmental factors, (ii) it requires oxygen, and (iii) it is an acidifying process. The organisms primarily responsible for these steps are the aerobic autotrophic bacteria *Nitrosomonas* and *Nitrobacter* (Alexander, 1977). In contrast with the heterotrophic soil organisms, whose source of C and energy are plant residues and soil organic matter, the autotrophs use CO_2 for C and obtain energy directly from the oxidation reactions. Since these two groups of bacteria are solely dependent on the supplies of NH_4^+ and NO_2^- for growth, it is apparent that the amount of these substrates governs their number and consequently the oxidation rate. When an ammonium fertilizer is added to a soil an initial lag phase is often observed in the nitrification process. This does not usually occur during nitrification of the low levels of N released by

ammonification of the soil organic matter. The delay in oxidation of fertilizer N can occur at the NH_4^+ to NO_2^- step or the NO_2^- to NO_3^- step, although normally the conversion of NO_2^- to NO_3^- is rapid and only traces of NO_2^- occur in soils. The lag is usually attributed to insufficient numbers of nitrifying organisms resulting from specific inhibitors (see chapter 8 of this book), from high levels of NH_3, or from high salt concentrations. The delay in nitrification is not a long-term effect; rather, it is a temporary event during the overall process of oxidizing NH_4^+ to NO_3^-. Nevertheless, these delays do affect the reactions of N fertilizers with soils (see later discussion of NO_2^- reactions in soils).

1. pH and Nitrification

Nitrification can take place over a pH range of about 5 to 10, but it is most rapid near pH 7 and is markedly reduced at a pH < 5.5, although the lower limit varies with the soil texture and the native organisms (Alexander, 1977). Since nitrification produces acids, it is not uncommon to see nitrification rates decline with time, especially in poorly buffered sandy soils fertilized with acidic N sources such as ammonium sulfate. The slower nitrification rate in strongly acid soils is primarily due to slower growth of the bacteria, but some believe it may be due to greater loss of N from chemical decomposition of NO_2^- in acid environments (Allison, 1973).

The ammonium oxidizers, *Nitrosomonas*, have an optimum pH in the alkaline range (ca. pH 7 to 9), while the nitrite oxidizers, *Nitrobacter*, prefer a neutral to slightly alkaline environment (ca. pH 6.5 to 7.5) (Alexander, 1977; Frederick & Broadbent, 1966). Under acid or neutral conditions, NO_2^- does not accumulate; when pH values exceed 8 and NH_3 levels are high, *Nitrobacter* activity may be restricted, which causes a temporary accumulation of NO_2^-. As noted above (section V A 2), these conditions frequently occur in an anhydrous NH_3 injection zone or in the microsite around a urea granule. With time, the NO_2^- will diffuse away from this area and become oxidized or will undergo various reactions associated with HNO_2, except, perhaps, in certain highly calcareous soils where NO_2^- is long-lived (Russell, 1961). Nitrification of a localized NH_3 or urea application begins at the outside edge, where NO_3^- is readily produced, and proceeds toward the center of the zone where NO_2^- may have temporarily accumulated. Eventually, the NH_3 is oxidized to NO_3^- and the accompanying acidity will lower the pH below its initial value, depending on the soil buffering capacity (Frederick & Broadbent, 1966; Pang et al., 1973; Wetselaar et al., 1972).

2. Soil Water, Aeration, and Nitrification

The nitrifying bacteria have an absolute requirement for oxygen, (since they are obligate aerobes) as well as certain demands for water. The precise relationship between nitrification and soil water content/aeration is difficult to assess because of the complex interrelations between soil gas transport, soil water content, and biological activity. However, research indicates that reducing the oxygen concentration from 20 to 11% does not

appreciably change the nitrification rate, but a further reduction to about 2% reduces nitrification by 50% and < 2% oxygen nitrification is negligible (Amer & Bartholomew, 1951). As soil water content increases above field capacity, nitrification declines sharply and with complete water logging nitrification ceases, except for a small amount at the soil surface. Below field capacity, nitrification continues over a wide range of soil moistures extending nearly to the wilting point, with the optimum in the range from 70 to near 100% of field capacity (Allison, 1973; Tisdale & Nelson, 1975).

3. Temperature and Nitrification

Nitrification is strongly affected by temperature, with maximum rates occurring between 30 and 35° C (Alexander, 1977). Frederick and Broadbent (1966) summarized the temperature-nitrification relation by noting that at 5, 10, 15 and 20° C nitrification was 10, 20, 50, and 80%, respectively, when compared with the 25° C nitrification rate. However, soils vary considerably in their nitrification rate since some soils have nitrification rates near 100 kg N/ha per week at 5° C (Sabey et al., 1959). Nitrification probably occurs at freezing temperatures and it appears that oxidation of NO_2^- is slowed more by decreasing temperatures than NH_4^+ oxidation (Black, 1968).

Interest in the temperature-nitrification relations has been stimulated by continued questions about the feasibility of fall fertilizer applications. As indicated above, however, nitrification can be substantial, even at cool soil temperatures. Nitrate produced during the autumn, when there is little plant growth, is more likely to be lost by leaching or denitrification than nitrate produced when a crop is actively growing during spring or summer. Field studies often show that fall-applied N is utilized less efficiently than N applied shortly before the growing season or during the growing season (Welch et al., 1971; Stevenson & Baldwin, 1969; Nelson & Uhland, 1955). Nitrification inhibitors offer the prospect of reducing these overwinter losses under certain conditions (Hergert & Wiese, 1980; Nelson & Huber, 1980; Touchton & Boswell, 1980; also see chapter 8 of this book).

4. Nitrification and Nitrogen Source, Placement, and Particle Size

The N source, placement, and particle size can also influence nitrification. As noted above, alkaline N sources (anhydrous NH_3, urea, diammonium phosphate) usually have an associated high pH and high NH_3 zone near the fertilizers, which can reduce nitrification rates and may even cause nitrites to temporarily accumulate. Acidic N sources (ammonium sulfate, ammonium nitrate, monoammonium phosphate) can affect nitrification in a similar manner in certain alkaline soils (Broadbent et al., 1957; Bezdicek et al., 1971), but more common occurrences would be delayed nitrification rates from (i) salt effect (Wetselaar et al., 1972; Hauck & Stephenson, 1965) and (ii) the reduced pH associated directly with the N source or from the acidity produced during nitrification (Broadbent et al., 1957; Hauck & Stephenson, 1965; Nommik, 1966). The particle size also affects nitrifica-

tion somewhat, with nitrification rates generally decreasing as particle size increases (Hauck & Stephenson, 1965; Nommik, 1966). The above effects are enhanced by fertilizer management practices that concentrate the fertilizer in a small volume of soil so that the fertilizer dominates the soil-fertilizer interaction, e.g., large granules or band fertilizer applications. The delayed nitrification rates discussed above are usually of a transitory nature and under normal conditions nitrification is complete within several weeks.

5. *Nitrification and Soil Mineralization-Immobilization*

Nitrification of fertilizer N can also be affected by the microbial mineralization-immobilization process, which is continuously occurring in soils. The balance between mineralization and immobilization is greatly affected by the proportion of C and N (i.e., the C/N ratio) in the substrate undergoing microbial decomposition; other factors such as quantity of organic matter, soil pH, and environmental factors can also affect it. Substrates rich in N emphasize the mineralization phase, which results in a net NO_3^- production, while substrates low in N emphasize the immobilization phase which may readily deplete the soil mineral N pool and therefore delay nitrification (Alexander, 1977; Black, 1968). Commercial fertilizers take part in the mineralization-immobilization cycle, particularly ammonium sources, which are more readily immobilized than nitrate sources (Allison, 1973; Legg & Meisinger, 1982).

If a substrate with a low N content [e.g., corn stalks (*Zea mays* L.) or wheat straw (*Triticum aestivum* L.)] is being decomposed when N fertilizers are added, it is quite likely that a significant quantity of fertilizer N will be incorporated into organic N compounds that are only slowly available (Frederick & Broadbent, 1966). In the absence of recent residue additions, net mineralization is the dominant process. However, it should be realized that some immobilization takes place whenever a N fertilizer is added to soil, particularly an ammonium fertilizer (Frederick & Broadbent, 1966, Legg & Meisinger, 1982).

C. Gaseous Nitrogen Losses

Gaseous N losses constitute important N transformations in virtually all soil-crop systems. These losses primarily involve (i) denitrification, (ii) NH_3 volatilization, and (iii) other losses such as NO_2^- decomposition and nitrous oxide (N_2O) evolution during nitrification. These N transformations involve the interaction of several biological, chemical, and physical factors within the soil-air-water system, which are difficult to describe and control under experimental conditions. Under field conditions, the interrelations are not well understood and our present knowledge of the underlying principles controlling the processes is inadequate. Nevertheless, there is much evidence from field N balance studies, lysimeters, and laboratory studies to indicate the magnitude of such losses and to outline the conditions that promote such losses.

1. *Denitrification*

Denitrification is microbial respiration that uses nitrate or nitrite as the terminal electron acceptor and thereby reduces N to various gaseous products such as N_2 and/or N_2O (Alexander, 1977; SSSA, 1984). Losses from denitrification range from 0 to > 70%, although most reported values fall between 10 and 30% for customary N rates applied to field crops on well-drained soils (Legg & Meisinger, 1982; Hauck, 1981). The general sequence for denitrification is thought to be the following:

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

although soil microbiologists are not totally agreed on the precise pathway (Alexander, 1977; Firestone, 1982). Denitrifying bacteria are found in at least 12 different genera and are quite abundant in soils (Firestone, 1982; Knowles, 1981). Denitrifiers are facultative anaerobic bacteria and most obtain energy from oxidizing the soil organic C, although some can also oxidize inorganic chemical compounds such as S. Under aerobic conditions they use oxygen as the terminal electron acceptor, but under anaerobic conditions they use NO_3^- according to the above sequence.

Several factors determine the rate and extent of denitrification in soils. The denitrifying organisms must, of course, be present along with a supply of NO_3^-; but in addition, there are other factors such as the (i) supply of oxidizable energy, (ii) aeration, (iii) soil pH, (iv) soil temperature, and (v) plants.

a. Energy Sources and Denitrification—Many investigators have observed that denitrification generally increases as soil organic C increases; denitrification is often negligible in soils containing < 1% organic C (Bremner & Shaw 1958a, b; McGarity, 1961). This general relation exists because organic C is the chief source of electrons used to reduce nitrate and because C oxidation also decreases the soil oxygen supply. The source of C could be the native soil organic matter or an organic amendment (e.g., manure, which has been shown to markedly increase gaseous loss of fertilizer N [Rolston et al., 1978]). However, the important factor is not necessarily the total C content but rather the biologically available C. Easily decomposed compounds, such as simple sugars, promote denitrification more readily than more lignified sources such as straw or corn stalks. Laboratory studies have shown that the level of water-soluble C is strongly related to denitrification (Bremner & Shaw, 1958b; Burford & Bremner, 1975; Stanford et al., 1975b). If denitrification is intermittent under field conditions, it is quite likely that the level of soluble C will determine the short-term denitrification rate.

b. Aeration and Denitrification—The soil oxygen supply is a major controlling factor in denitrification. Low soil oxygen levels result in an increase in the synthesis and activity of denitrifying enzymes and also affect the supply of NO_3^- by slowing nitrification (see above). Concentrations of dissolved oxygen need to be quite low, approximately < 0.2 ppm, before

denitrification begins (Greenwood, 1962; Woldendorp, 1968). Soil water content, as such, has little effect on denitrification, but it greatly influences the oxygen diffusion rate since oxygen diffuses through water 10 000 times slower than air. Because of this, denitrification is not normally a problem in soils drier than about 80% of field capacity. Several complex factors influence denitrification, such as total soil porosity (influenced by texture and aggregation), length of the oxygen diffusion path (influenced by water content and aggregate size), and the oxygen consumption rate of the soil. In nature the situation is further complicated by the fact that soil organic matter is not uniformly mixed throughout the soil but is present as pieces of root or residue debris. It has generally been accepted that soils can simultaneously have well-aerated zones near air-filled pore spaces and poorly aerated zones near the center of large aggregates or near rapidly decomposing organic matter. The proportion of the well-aerated vs. the poorly aerated zones can be affected by seemingly minor changes in the soil water content or oxygen consumption rate. For example, a rain shower or irrigation can readily trigger denitrification losses (Ryden & Lund, 1980).

Aeration also affects the proportion of N_2O and N_2 produced. The dominant product is N_2 under strictly anaerobic conditions, but the proportion of N_2O usually increases as the oxygen stress decreases. It is evident from the foregoing discussion that soil denitrification is favored by poor aeration, but poor oxygen supplies may occur in several ways: (i) through long-term, large-scale flooding, e.g., poorly drained soils or paddy culture; (ii) through a long-term, small-scale process associated with an anaerobic microsite surrounded by an aerobic soil, e.g., the zone surrounding decomposing organic matter; or (iii) through a short-term, large-scale process produced from temporary periods of poor aeration, e.g., gaseous losses associated with rainfall or irrigation. The largest potential denitrification losses occur in very wet soils that have an abundant supply of available C.

c. Soil pH and Denitrification—It is not possible to precisely define the relation between denitrification and pH for all soils due to the diversity of the denitrifying organisms and the potential changes in soil pH under waterlogged conditions. However, it is generally observed that the soil reaction has little effect on denitrification between pH 6 and 8; as the pH drops < 5, denitrification usually decreases markedly (Bremner & Shaw, 1958b; Burford & Bremner, 1975; Firestone, 1982), although soils are frequently encountered with significant denitrifying activity $<$ pH 5 (Ekpete & Cornfield, 1965; Gilliam & Gambrell, 1978). Soil acidity also affects the composition of the gaseous products, i.e., the relative abundance of N_2O vs. N_2. Above pH 6, N_2 is usually the predominant gaseous product with some N_2O given off during the early stages of denitrification. As the pH falls < 6, the proportion of N_2O increases with N_2O often becoming the dominant product when soil pH is ≤ 5 (Alexander, 1977; Firestone, 1982).

d. Temperature and Denitrification—Since denitrification is a microbial process, it is markedly affected by temperature with the optimum usually near 30° C. From 10 to 30° C, denitrification rates increase steadily with

the 10° C rate often being about one-half the 20° C rate, which in turn is about one-half the 30° C rate (Bremner & Shaw, 1958b; Cho et al., 1979; Stanford et al., 1975a). Below 10° C, denitrification decreases rapidly and the reported lower limits vary from 2 to 10° C, depending on factors such as incubation technique, oxygen demand, and available C (Bremner & Shaw, 1958b; Cho et al., 1978; Gilliam & Gambrell, 1978; Stanford et al., 1975a). Below 2° C, denitrification is negligible.

e. Plants and Denitrification—Plants may either increase or decrease denitrification, depending on the particular soil factor limiting denitrification such as available C, oxygen supply, or NO_3^- level. Plants increase denitrification by (i) consuming oxygen through root respiration, (ii) releasing readily available C through exudation and sloughing of root tissue, and (iii) by maintaining a high microbial population in the rhizosphere. They can reduce denitrification by (i) removing NO_3^- through crop uptake, (ii) removing NH_4^+, which could readily be converted to NO_3^-, (iii) reducing the soil water content, which improves the oxygen supply, and (iv) directly increasing oxygen availability in the rhizosphere of plants that transport oxygen, such as paddy rice. Research evidence supports both of the above views, i.e., plants may either enhance or hinder gaseous N losses.

Allison (1955) used data from several lysimeter experiments and concluded that plants generally promoted N losses. He estimated the average gaseous loss to be about 20% from 51 cropped lysimeters, while comparable uncropped lysimeters lost about 12%. Stefanson & Greenland (1970) and Stefanson (1972b) grew plants in gas-tight chambers and found that cropping enhanced denitrification losses when the soil water content was 50 to 80% of field capacity. Later work also showed greater gaseous N losses with plants, particularly when nitrate sources were added to soils near field capacity (Stefanson, 1972 a,c) and to soils with low available C (Stefanson, 1976). Similar findings of greater gaseous N losses with crops have been reported by Rolston et al. (1978) and by Volz et al. (1976), who used instrumental field microplots. Woldendorp (1968) and Smith and Tiedje (1979) concluded that denitrification is stimulated in the vicinity of plant roots, particularly when NO_3^- levels are high.

Other researchers have found that plants either decrease or have little effect on gaseous N losses. Carter et al. (1967) used field microplots and recovered 92% of the added ^{15}N fertilizer on fallow plots as compared with a 94% recovery on plots cropped to sudangrass [*Sorghum Sudanense* (Piper) Stapf]. Craswell and Strong (1976) also used ^{15}N in microplots and reported that wheat was an effective N conservation agent because of its direct N uptake and its depletion of soil water. Similar fertilizer N recoveries were observed in fallowed and cropped plots by Kowalenko and Cameron (1978). Smith and Tiedje (1979) showed that plants can effectively reduce denitrification when NO_3^- concentrations are low. It is also noteworthy that although Stefanson usually observed greater N losses with plants, this effect was not observed with undisturbed soil cores (Stefanson, 1972d).

Under field conditions, the above plant effects interact with soil properties that limit denitrification and with the type of denitrification event

(e.g., large scale flooding vs. periodic poor aeration) to produce the final gaseous N output. The end result of these complex processes is difficult (some would say impossible) to predict; however, the prevailing opinion seems to be that denitrification rates are increased by plants because denitrification in most fertilized soil-crop systems is C-limited.

2. *Ammonia Volatilization*

Ammonia volatilization is a major avenue for N loss for topdressed ammonium sources on calcareous soils, for surface-applied urea on acid or alkaline soils, and for anhydrous NH_3. Ammonia volatilization is a complex process affected by several interacting chemical and physical factors as well as soil, fertilizer management, and environmental factors. Under some conditions, losses of 50% may be encountered but more common values would be 5 to 20%, depending on several factors discussed below (Nelson, 1982; Freney & Simpson, 1981).

a. General Principles—Ammonia losses from anhydrous NH_3 result from its rapid conversion from a liquid to a gas during and after injection. These losses can usually be avoided by applying it at a sufficient depth and under appropriate soil physical and moisture conditions that ensure a rapid closure of the injection channel.

Ammonia losses from urea occur readily because urea is enzymatically hydrolyzed to ammonium carbonate [$(NH_4)_2CO_3$] through the ubiquitous enzyme urease. Ammonium carbonate readily decomposes to produce NH_3 and CO_2 according to the following reaction:

$$H_2N\text{-}CO\text{-}NH_2 \xrightarrow[H_2O]{\text{urease}} (NH_4)_2CO_3 \begin{cases} \xrightarrow{-H_2O} 2NH_3 + CO_2 \\ \xrightarrow{+H_2O} 2NH_4^+ + OH^- + HCO_3^- \end{cases} \quad -2H_2O \qquad [3]$$

The proportion of NH_3 to NH_4^+ is determined by the local pH (Fig. 7–4). An ammonium carbonate solution has a pH of about 8.6 (Hauck & Stephenson, 1965), which sets the stage for large NH_3 losses from hydrolyzed urea whenever the NH_3 is free to escape to the atmosphere (e.g., surface applications). Such losses can be particularly large for urea topdressed on meadows or small grains and should be expected on either acid or alkaline soils due to the high microsite pH surrounding a urea granule (Freney & Simpson, 1981; Nelson, 1982; Terman, 1979).

When ammonium fertilizers are applied to calcareous soil, the solubility of the calcium salt formed from the anion accompanying NH_4^+ must also be considered as shown below:

$$NH_4X + CaCO_3 \rightarrow CaX + (NH_4)_2CO_3 \begin{cases} \xrightarrow{-H_2O} 2NH_3 + CO_2 \\ \xrightarrow{+H_2O} 2NH_4^+ + OH^- + HCO_3^- \end{cases} \quad -2H_2O \qquad [4]$$

If CaX is insoluble (e.g., if X were SO_4^{2-} or HPO_4^{2-}), the reaction favors production of ammonium carbonate and subsequent decomposition to NH_3. If CaX is soluble (e.g., if X were NO_3^- or Cl^-), then ammonium carbonate formation is not favored and NH_3 losses are greatly reduced (Fenn & Kissel, 1973; Terman, 1979). Ammonia losses from monoammonium phosphate and ammonium polyphosphate are thought to be low due to the formation of metastable reaction products such as $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$ and $Ca(NH_4)_2P_2O_7 \cdot H_2O$ (calcium diammonium phosphate and calcium ammonium polyphosphate) (Terman & Hunt 1964; Terman, 1979).

Ammonia losses also occur quite readily if N fertilizers are added to the floodwaters of paddy rice. Reported losses for urea are as high as 20 to 50% while ammonium sulfate losses are often less (Vlek & Craswell, 1979; Mikkelsen et al., 1978). The extent of these losses are governed by the floodwater pH, which, in turn, is related to aquatic photosynthesis and respiration as well as the chemistry of the N source. The pH of the paddy water may reach 9.5 or 10 near midday due to CO_2 assimilation, but it can drop to about neutrality at night due to CO_2 released from respiration.

b. Factors Affecting Ammonia Losses—Ammonia volatilization is a complex process involving chemical reactions within the soil, physical transport out of the soil, and biological interactions within the soil. It is not surprising that NH_3 losses are influenced by a number of factors such as soil pH, soil CEC, calcium carbonate ($CaCO_3$) content, temperature, water loss, and the rate and method of N fertilizer application.

Ammonia losses generally increase as soil pH increases, but significant losses can also occur on acid soils when urea or other non-acid-forming N sources are applied on the surface. The pH immediately surrounding the fertilizer reaction zone is most important. Soil pH values > 7.0 increase NH_3 losses by increasing the NH_3/NH_4^+ ratio (Fig. 7–4). Soil CEC affects NH_3 losses by serving as a temporary sink for NH_4^+, which reduces the aqueous NH_4^+ concentration and the NH_3 concentration. It is commonly found that NH_3 losses are greatest on low CEC soils (coarse texture, low organic matter) and least on high CEC soils (fine texture, high organic matter) (Freney & Simpson, 1981; Nelson, 1982; Terman, 1979).

The soil calcium carbonate content affects NH_3 loss by affecting the soil pH as well as the mechanism of N loss through possible precipitation of the NH_4^+ fertilizer reaction products (see above equations). Woldendorp (1968) presented results from 176 soils throughout the world, which showed that NH_3 losses were more related to calcium carbonate content than the soil pH. High temperatures also favor NH_3 losses by increasing the hydrolysis rate of urea fertilizers, by increasing the NH_3/NH_4^+ ratio, by decreasing the solubility of NH_3 in water, and by increasing gaseous diffusion rates. Equations [3] and [4] above suggest that NH_3 losses should be encouraged by water loss and research has generally demonstrated that NH_3 losses do increase as drying conditions intensify (low humidity or high temperature). Lastly, the rate and method of N application affect losses with high N rates and surface applications favoring losses. Incorporating N

sources at least 5 cm into the soil greatly reduces or eliminates losses. Ammonia losses are often greatly decreased by relatively small water additions, which may transport a N source deeper into the soil where it can be adsorbed. This is especially true for urea since it is readily leached before hydrolysis (Freney & Simpson, 1981; Nelson, 1982; Terman, 1979).

In summary, NH_3 losses are greatest with (i) surface-applied fertilizers, (ii) under environmental conditions that favor drying, (iii) high pH, and (iv) in soils with a reduced capacity to absorb NH_3 or NH_4^+.

3. Other Gaseous Losses

Other possible avenues of gaseous N loss include the evolution of N_2O during nitrification, the self-decomposition of nitrous acid (HNO_2), and the reaction of nitrous acid with various soil constituents such as organic matter, transition metals, clay minerals, and ammonium and amino groups (Allison, 1973; Nelson, 1982; Woldendorp, 1968). Nelson (1982) recently reviewed these mechanisms, as well as their supporting evidence, and concluded that the most likely mechanisms are the self-decomposition and reactions of nitrous acid with organic matter and the evolution of nitrous oxide during nitrification.

The self-decomposition of nitrous acid produces nitric oxide (NO) and nitrogen dioxide (NO_2), which may be volatilized from the soil or react within the soil to produce NO_3^-. Decomposition of nitrous acid requires an acid environment because the pk_a of the acid is 3.2 and only about 2% of the NO_2^- is present as HNO_2 at pH 5. Acid soils would obviously promote decomposition, but Nelson (1982) has also postulated that the surface of clay minerals would also be a likely environment since the pH there is often 2 pH units lower than the bulk soil solution. Researchers do not agree on the importance of N losses due to HNO_2 decomposition. Some feel that most of the N is retained through oxidation to NO_3^- (Allison, 1973; Broadbent & Clark, 1965) while others feel that such losses are quite important (Nelson, 1982).

The reaction of nitrous acid with soil organic matter involves both liberation of N gases and the fixation of N into slowly available forms. The phenolic substances in soil organic matter have been shown to be largely responsible for the production of N_2 and N_2O with losses being as much as 20% (Bremner & Nelson, 1968; Nelson & Bremner, 1970). Other work has shown that NO_2^- can react with the lignin-derived fraction of soil organic matter in a wide range of soils and form relatively resistant organic compounds (Nelson & Bremner, 1969). There seems little doubt that NO_2^- can react with organic matter to produce N gases or stable organic N complexes, but the extent of these reactions under field conditions remains uncertain.

Small amounts of nitrous oxide can also be evolved during the biological oxidation of NH_4^+ to NO_2^- by *Nitrosomonas* in aerobic soils (Bremner & Blackmer, 1978; Blackmer et al., 1980). These losses increase with an increase in the NH_4^+–N concentration. Fertilizer N losses under field conditions have been as high as 5% with anhydrous NH_3, while losses from ammonium sulfate and urea were < 1% (Bremner et al. 1981). The nitrous oxide losses from anhydrous were greatest between the second and fourth week after application.

Many questions remain about the practical importance of the above NO_2^- losses under field conditions. Since NO_2^- accumulates most easily in alkaline environments, it seems unlikely that the nitrous acid reactions could account for significant N losses. However, it has already been pointed out that NO_2^- frequently accumulates around urea particles and around the anhydrous NH_3 injection channel; this NO_2^- could diffuse into the surrounding acid soil (made more acid by nitrification) and then be lost through one of the mechanisms discussed above. The extent of field nitrous oxide loss during nitrification is also an open question; it appears that such gaseous losses can be significant for anhydrous NH_3. Much more research is needed to determine the extent and magnitude of N losses under field conditions.

D. Nitrogen Losses Through Water Transport

Nitrate-N is readily transported in water due to its high solubility and its nonadsorption on the soil exchange complex. It is subject to loss in the surface runoff and in the water percolating through the soil.

Legg and Meisinger (1982) concluded that soluble N losses through surface runoff are generally very small, except when high rates of fertilizer are surface-applied just before large rainfall events. In many cases, the gain of N in the precipitation is greater than the soluble N lost in the runoff.

There is general agreement that N leaching is often the major avenue of N loss from field soils in humid climates (Allison, 1973; Legg & Meisinger, 1982). Leaching losses occur when (i) the soil contains significant quantities of NO_3^-–N and (ii) water is moving downward through the soil. A number of factors influence these two prerequisites, such as (i) rate, time of applications, and source of N; (ii) crop growth and N uptake; (iii) soil characteristics that affect quantity and type of percolation; and (iv) the quantity, pattern, and time of water inputs.

The major fertilizer management practices that affect leaching are the rate and time of N application. If N rates are at or slightly below the crop assimilation capacity, the crop is usually a good sink for N (Fig. 7–5). However, soil nitrates accumulate quite readily once N rates exceed the crop assimilation capacity (Herron et al. 1968; Broadbent & Carlton, 1978). Time of N application also affects leaching. Nitrogen applied well before the period of crop uptake (e.g., fall-applied N) is subject to greater leaching losses than N applied just before crop uptake (Stevenson & Baldwin, 1969; Welch et al., 1971). The source of N can also influence the short-term leaching losses, since NO_3^- sources are subject to immediate loss and NH_4^+ sources must be nitrified first. However, N source is usually not a major long-term factor, since the NH_4^+–N is usually nitrified in a few weeks and factors such as crop uptake, N rate, and timing will determine the overall leaching losses in upland soils.

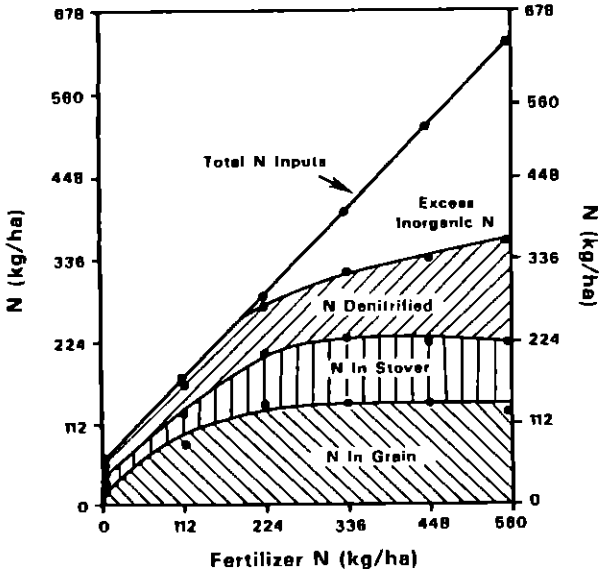


Fig. 7–5. Compartmentalization of N in a corn plant-soil system as influenced by fertilizer N rates (Broadbent & Carlton, 1978; Legg & Meisinger, 1982).

Crop N uptake is indirectly related to N leaching because crop uptake is usually the largest N reservoir and as more N is utilized by the crop, less remains for leaching. Using adapted, high-yielding varieties and maintaining adequate soil fertility will thus decrease leaching by increasing crop utilization. Cover crops grown between cropping seasons will also reduce leaching (Allison, 1955, 1973).

Assuming that NO_3^-–N is present in the soil, the major factor affecting leaching is soil water percolation. Soil nitrate leaching has often been conveniently described as *piston flow* or *complete displacement*, but field observations frequently indicate that this description is inadequate. Water percolation often involves a rapidly moving portion of water that penetrates deeply into the soil through large pores and by-passes much of the soil solution. Interconnected with this large-pore water is the small-pore water, which is also displaced downward during percolation, but at a slower rate. As water and NO_3^--N percolate through soil, a portion will appear relatively deep in the soil, but the greatest concentration of NO_3^--N will usually be much shallower (Boswell & Anderson, 1964; Thomas & Phillips, 1979). Viets and Hageman (1971) suggest the generalization that the maximum NO_3^-–N concentration will advance about 30 cm for each 30 cm of water infiltration. In multipore soil systems, the peak NO_3^-–N concentration advances like a broad wave, which widens and becomes more diffuse as it moves deeper into the soil. Several soil properties affect the type of percolation (multipore vs. piston flow) and the quantity of percolation. For example, soil structure, clay type, soil texture, and organic matter content affect the pore size, pore continuity, and soil texture affects the water holding capacity. Coarse-textured soils are more vulnerable to

leaching due to their low water holding capacity and the greater likelihood of piston flow (low clay and organic matter contents, poor structure). Other soil properties that affect N leaching are the water infiltration rate and textural discontinuities in the profile.

Leaching usually increases as the quantity of percolating water increases. Water percolation, in turn, is determined by the balance between water added through precipitation and infiltration and water lost through evaporation and transpiration (ET). During the growing season, water use through ET exceeds water inputs and percolation is negligible, except on soils with low water holding capacities and in high-rainfall or high-irrigation areas. During the winter months, water inputs in humid areas exceed ET and leaching is common (Allison, 1973; Chichester, 1977; Chichester & Smith, 1978). This general leaching pattern is modified by local factors such as soil freezing, irrigation practices, soil water holding capacities, and the type of soil water percolation. Thus, it is generally true that percolation is most likely over winter and will usually increase as the precipitation increases, but how effective this participation is in leaching NO_3^-–N below the crop root zone will depend on local factors such as soil freezing and the extent of large-pore water movement.

E. Acidity and Basicity of N Sources

Nitrogen fertilizers can increase, decrease, or leave soil pH unchanged depending on (i) whether the form of N is NH_4^+ or NO_3^-, (ii) the accompanying anion or cation, (iii) the crop grown, and (iv) the ultimate fate of the fertilizer N. Ammonium sources produce acidity during nitrification (see Eq. [2]) and the theoretical acidity is equivalent to 3.6 kg $CaCO_3$/kg N. The final acidity may be greater if the NH_4^+ is associated with an acidic anion such as sulfate (SO_4^{2-}). Thus, ammonium sulfate is usually the most acidic N source. Nitrate sources accompanied by basic cations such as Na^+ or Ca^{2+} may raise the soil pH. The crop grown can affect pH through its uptake of basic cations relative to acidic ions. Pierre and Banwart (1973) have shown that the aboveground portion of the common field crops take up about 0.5 equivalent of excess base per equivalent of N, but most cereal grains removed < 0.1 equivalent of excess base per equivalent of N. This means that the actual nitrification acidity may only be about 50% of the theoretical value (or 1.8 kg $CaCO_3$/kg N) if the entire crop is removed and < 10% of the theoretical value if only the grain is harvested. The fate of the added N also affects the acidity. Nitrified N left in the soil or leached out would produce the full theoretical acidity, while N lost in denitrification will nullify the acidity (Pierre & Banwart, 1973; Pierre et al., 1970, 1971).

A procedure was proposed by Pierre (1933) for estimating the potential acid- or base-forming tendencies of a given fertilizer based on its content of acidic anions (SO_4^{2-}, Cl^-), basic cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), and the crop uptake of acid and basic ions. This approach predicts that ammonium nitrate, urea, anhydrous NH_3, or solutions of these materials possess an equivalent acidity of about 1.8 kg $CaCO_3$/kg N, while ammonium

sulfate and monoammonium phosphate require about three times as much calcium carbonate. These figures, however, should be used for relative comparisons among sources rather than accurate forecasts, because the above discussion has clearly shown that one cannot accurately predict the degree of acid formation under field conditions. Field research indicates that about 30% of the theoretical acidity developed on plots receiving an average annual N rate of 160 kg N/ha; 60% of the theoretical acidity developed on heavily fertilized plots, probably due to greater leaching losses on the over-fertilized plots (Pierre et al., 1971).

Another facet of N fertilizer acidity occurs with no-till systems. Since N sources are broadcast on the surface and the soil is not mixed by tillage, a highly acidic surface layer often develops (Blevins et al., 1977). The pH may be lowered as much as 1 pH unit in the surface 5 cm, which can inactivate surface-applied triazine herbicides. The acidifying effect of N fertilizers must therefore be carefully considered in modern agriculture.

VI. USING NITROGEN FERTILIZERS

Nitrogen plays a central role in modern agriculture. It is an essential nutrient and it is also the major limiting nutrient in most agricultural soils growing nonleguminous crops. Nitrogen is an energy-intensive input; the energy invested in 7 kg of N is equivalent to the energy in 8 L of diesel fuel (i.e., 1 gallon of diesel fuel equals about 7.3 pounds of N; Lockeretz, 1980; Cervinka, 1980). Nitrogen fertilizer often accounts for about 30% of the energy budget of a modern, nonirrigated corn production system (Mitchell & Teel, 1977). Increasing costs of energy have underscored the need for improving N uptake efficiencies, which are greatly affected by N rate, source, timing, and application method.

A. Determining Nitrogen Needs

Procedures for determining N fertilizer needs rest on N-balance principles, which have recently been reviewed by Meisinger (1984). There are two broad approaches, but, in general, they both reveal that (i) N fertilizer needs are directly related to the crop N requirement, (ii) fertilizer needs are indirectly related to the N use efficiency, and (iii) the N supplied from the soil through mineralization and residual mineral N should also be taken into account in the general case.

1. Determining Crop Nitrogen Requirements

The crop N requirement is involved in determining N fertilizer needs, because the crop is a major N consumer and assimilates anywhere from 30 to 70% of the fertilizer N applied. Nonleguminous crops are known to vary in their N needs. Crops that produce large amounts of dry matter generally need more N than lower producing crops; thus, small grains usually require less N than corn. The likely dry matter production of a given crop is therefore an important input in determining N needs.

The internal crop N requirement can be defined as the N concentration in the total aboveground dry matter at near-maximum yield. The internal crop N requirement seems fairly constant over a range of environmental and cultural conditions (Stanford, 1966, 1973). Therefore, it can serve to forecast the total N needs for a given total dry matter production. The internal N requirements have been estimated for several crops as follows: about 12 g N/kg (1.2%) for corn (Stanford, 1966, 1973), about 12.5 g N/kg (1.25%) for wheat (Stanford & Hunter, 1973), and about 16 g N/kg (1.6%) for the whole plant of sugarbeets (*Beta vulgaris* L.) (Carter et al., 1976; Stanford et al., 1977).

The final estimate of the crop N needs can be made by multiplying the expected total dry matter production by the internal N requirement. For example, corn contains about 50% of its total dry matter in the grain so an expected yield of 10 metric tons/ha at 15.5% moisture would require about 200 kg N/ha. Of course, precise knowledge of yield for the coming year is not possible, but most farmers/advisors can forecast yields accurately enough based on past yields, current management practices, and some measure of available water obtained from direct soil measurements or the likely rainfall of an area. The overall objective is to estimate N needs with sufficient accuracy so that fertilizer N can be added to meet crop needs, but not to fertilize the crop beyond the assimilation capacity, which leads to a marked reduction in N use efficiency.

2. Estimating the Soil Nitrogen Supply

Once the crop N needs have been estimated, the soil N supply should be assessed to determine the amount of supplemental N fertilizer needed. The only case where a soil N assessment can be overlooked is when the soil-crop system is at steady-state soil N levels, in which case the fertilizer needs can be predicted from the crop N removals and the total recovery efficiencies (Meisinger, 1984). Steady-state conditions, however, are long-term approaches that neglect annual fluctuations in available soil N. Furthermore, they are difficult to justify experimentally. Soil scientists have therefore had a long-term interest in methods of evaluating available soil N. The available soil N pool can be divided into two components: an inorganic component composed mainly of residual NO_3^-–N and an organic component that is mineralized throughout the growing season.

a. Residual Mineral Nitrogen—The soil mineral N content was formerly considered to be of little value toward estimating available soil N due to sampling difficulties and the transitory nature of the soil NO_3^-–N pool. Many field investigations, however, have indicated that the soil mineral N pool significantly affects crop yield and should be considered when estimating the soil N supply. Spring NO_3^-–N evaluations are especially useful when (i) previous N inputs have exceeded the crop assimilation capacity due to large fertilizer or manure additions, (ii) crop N removals have been low due to droughts, disease, or practices such as summer fallowing, and (iii) N has not been leached below the root zone due to low percolation, large pore water movement, or deeply rooted crops. These conditions oc-

Table 7–4. Summary of N recommendation systems used in the USA for corn in selected states (Keeney, 1982; Meisinger, 1984).

State	Soil N analysis		Soil properties requested	Corn N factor†	N credits for		
	Mineral	Organic			Manure‡	Alfalfa§	Soybeans§
				kg N/metric ton		kg N/ha	
Colo.	NO_3^--N	OM	Texture	38	2.5	56	30
Neb.	NO_3^--N	None	Soil type	25	2	110	65
Iowa	None	None	Soil assoc.	27	2.5	156	45
Ill.	None	None	Soil type	25	2.5	110	45
Ind.	None	None	Soil type	25	None	80	20
Pa.	None	None	Soil type	21	2.5	136	None

† Kilograms N needed to produce 1 metric ton of dry grain.
‡ Kilograms N credit per metric ton of fresh manure.
§ Nitrogen credit if previous crop was a good stand of alfalfa or was soybeans.

cur most frequently in the western portion of the USA; consequently, soil NO_3^-–N tests have been readily adopted in that area (see Table 7–4).

Recommended NO_3^-–N procedures involve intensively sampling the root zone of a relatively uniform area of soil representing similar soil properties and management histories. Since NO_3^-–N is mobile, it is essential to sample below tillage depth and most desirable to sample the entire root zone; suggested depths are usually 120 cm or deeper. Samples are usually air-dried immediately after collection and are later extracted with a salt solution and analyzed for NO_3^-–N by a convenient method suited to large numbers of samples (N.C. Region Soil Test. Comm., 1975; Soltanpour et al., 1979; Weise & Penas, 1979). The soil NO_3^-–N is usually considered to be approximately equivalent to fertilizer N and suggested N rates are adjusted accordingly. Despite the large spatial variability of NO_3^-–N, and its accompanying sampling problems, it has been conclusively shown that a soil mineral N evaluation is an important component of available soil N in modern agricultural systems, particularly in subhumid areas. Its usefulness in humid areas has also been demonstrated under conditions such as low winter rainfall, deep soils, and large fall NO_3^-–N levels (Maples et al., 1977; Vander Paauw, 1962, 1963).

b. Soil Total Nitrogen Content—Soil total N tests are aimed at estimating mineralization by determining the size of the organic N pool. Rather than analyze for total N directly, most laboratories determine soil organic matter, which contains about 5% N and is an easier and quicker determination. Because a total analysis is involved, these procedures are not greatly affected by sample preparation or time of sample collection. Disadvantages of total analysis procedures stem from the fact that only a portion of the organic N becomes available to the crop during a particular growing season. The portion that becomes available is very difficult to predict because environmental factors such as temperature and moisture influence the amount of mineralization. Also, the addition of fresh organic matter provides a greater proportion of readily available N than the more stable soil N compounds. Nevertheless, several states currently use a total-

analysis procedure to estimate mineralization, usually by taking a fixed percentage of the organic matter, which amounts to a 1 to 3% annual mineralization rate (Keeney, 1982; Meisinger, 1984). Thus, although total analyses have not proved useful in making precise estimates of mineralization, they can provide a useful first approximation.

c. Biological Incubating—Incubation tests attempt to separate a more active component of the soil total N pool by employing the soil's own biological agents to oxidize the organic matter under controlled temperature and aeration conditions. Proposed tests employ temperatures ranging from 20 to 40° C and a wide range of aeration conditions that vary from well-aerated sand-soil mixtures to waterlogged anaerobic conditions. The suitability of such a wide range of incubation conditions stems from the fact that the most frequent rate-limiting step in mineralization is the breakdown of organic N to form NH_4^+, i.e., ammonification, which is carried out by many different organisms. Nitrification, however, is greatly affected by aeration so it is necessary to measure both NO_3^-–N and NH_4^+–N produced during the incubation.

Correlations between biological incubation procedures and greenhouse N uptake are usually good once soil NO_3^-–N has been taken into account. However, when testing proceeds to field conditions, the correlations are considerably lower, especially if field trials cover a range of climates, soils, or years (Keeney, 1982; Meisinger, 1984; Stanford, 1982). Biological tests are markedly affected by sample pretreatment, especially those involving short-term aerobic incubations. To obtain meaningful comparisons, it is necessary to carefully standardize sample preparation and incubation conditions. Recent investigations have shown that it may be possible to extend laboratory aerobic mineralization data to field temperature and water regimes, at least within a limited area (Stanford et al., 1977; Smith et al., 1977). This approach is less empirical, but is quite time consuming and is tied to average climatic conditions for predictive purposes. It is being further evaluated as a research approach to estimate mineralization.

The principal drawbacks to biological procedures are sample handling, pretreatment effects, and long processing times (at least 1-week incubations). The currently recommended biological index is the NH_4^+–N produced after 1 week of anaerobic incubation at 40° C (Keeney, 1982). Biological indexes were used in several statewide N recommendations systems 25 yr ago, but are not currently used in any state soil testing laboratory (Keeney, 1982; Meisinger, 1984). Nevertheless, it is generally recognized that biological incubations that measure the total mineral N production (NO_3^-–N plus NH_4^+–N) provide a good measure of the soil's mineralization ability.

d. Chemical Extractions—The goal of chemical extraction procedures is to chemically separate a portion of the active soil N pool from the large total N pool. Advantages of such an extractant would be a simple and rapid analysis, which would be compatible with P and K tests. With these advan-

tages in mind, it is not surprising that soil scientists have searched many years for a suitable extractant. Such a chemical extractant, however, has not been identified because soil N transformations are dominated by biological reactions, which strongly interact with the environment over time at any given location.

The range of extractants tested includes water, weak to strong salt solutions, mild acids and bases, and strong acids and bases with or without an oxidant. The extracted material has likewise been analyzed in a number of ways including C content, total N content, distillable NH_3, and absorption of ultraviolet radiation. The results of those strictly empirical procedures are usually influenced by sample preparation, sample drying, extraction time, and soil/extractant ratios.

Interest in basic and acidic extractions developed as a natural extension of the procedures used to fractionate soil organic matter based on differential solubilities in acids or bases. Various reagents are employed, e.g., sulfuric acid (Purvis & Leo, 1961; Richard et al., 1960), calcium hydroxide [$Ca(OH)_2$] (Prasad, 1965), and sodium hydroxide (NaOH) (Cornfield, 1960). Strong acids or bases attack a large portion of the soil organic N and the N removed by such treatments usually bears a close relation to the soil total N content. Such procedures, thus, have the same disadvantages as discussed above for total N analysis. Milder acidic or basic extractions have been evaluated in several studies, but have performed quite inconsistently (Jenkinson, 1968; Keeney & Bremner, 1966; Stanford, 1978a,b). Oxidizing agents (chromate or permanganate) have also been tested in acidic or basic solutions with the hope that they would selectively oxidize a biologically meaningful fraction of the organic matter (Nommik, 1976; Stanford, 1978a,b). The alkaline permanganate method has been widely tested but has given very inconsistent results (Keeney & Bremner, 1966; Stanford, 1978a; Stanford, 1982). More recently, oxidative procedures have been investigated under acid conditions with encouraging preliminary results (Stanford, 1978b), but the general applicability of these latest procedures is not known.

Most recent research has centered on mild extractants such as water or mild salt solutions, e.g., 0.01 *M* calcium chloride ($CaCl_2$). This approach is based on the observations and procedures of Livens (1959a,b) as modified by Keeney and Bremner (1966) and Smith and Stanford (1971). Keeney and Bremner (1966) considered the total N removed by a boiling water extract to be as good as a biological incubation method; furthermore, they found it was not subject to sample drying effects, which influenced the microbial method. The currently recommended method consists of an overnight (16 h) autoclaving in 0.01 *M* calcium chloride and subsequent determination of the NH_4^+–N released (Keeney, 1982). The method is rapid, is not greatly affected by sample pretreatment, and is amenable to automated analysis. But it has not been extensively evaluated under field conditions, although the field results to date are encouraging (Fox & Pickielek, 1978; Roberts et al., 1972). Workers in the USA are not employing a chemical extraction method to estimate mineralizable N, despite the large research effort that has gone into evaluating various methods.

e. Indirect Methods—Indirect methods involve documenting a local variable, which is linked to an increase in mineralization; examples include N credits for previous legume crops and recent manure additions. Legume N credits are used throughout the USA and range from 55 to 155 kg N/ha for previous alfalfa crops (*Medicago sativa* L.) (depending on stand and years since alfalfa) and from 20 to 55 kg N/ha for prior soybean [*Glycine max* (L.) Merr.] crops (Table 7–4). Manure N credits are about 2.5 kg N/metric ton of manure (approximately 5 pounds N/2000 pounds manure). Indirect methods are easy to use and have generally performed well as initial broad-scale adjustments for the soil N supply.

3. Estimating Nitrogen Uptake Efficiency

The final factor to consider in estimating N fertilizer needs is *N utilization efficiency*. This term must be carefully defined since at least two definitions are in general use (Meisinger, 1984). The first is defined through the N uptake in the aboveground portion of the crop, which commonly varies between 40 and 60%; the second is defined through the N recovered within the whole soil-crop-root system and commonly varies between 65 and 85%. The distinction becomes important when considering methods to estimate these terms and in applying these terms to conceptual soil-crop systems.

Fertilizer efficiencies are functions of several interacting N transformations such as leaching, denitrification, and NH_3 volatilization, as well as several management variables such as N source, placement, and timing. It has not been possible to predict these parameters from first principles. Soil scientists have therefore approached this problem empirically by estimating fertilizer efficiencies over a range of soil and climatic conditions. The end result is that efficiencies can usually be estimated in a general sense, but one cannot accurately predict the efficiency for a specific soil-crop system. Obviously, further research is needed to investigate factors affecting fertilizer efficiency to better predict this parameter for specific locations.

4. Recommendations for Nitrogen Use on Crops

Before a N recommendation system can be established, one must carefully define the boundaries of the soil-crop system in time and space and also assess the sources of variation that underlie varying N fertilizer needs (e.g., crop differences, soil NO_3^-–N levels). Nitrogen recommendation systems should systematically combine the above components of crop N requirements, soil N supply, and N utilization into a working N advisory system that supplies N in quantities sufficient to meet the crops needs and in a manner that leads to high crop utilization. Excessive N inputs should be avoided since they inevitably lead to environmental impacts and inefficient N use.

When defining the soil-crop system, scientists have basically chosen either the *aboveground* approach or the *whole-crop* approach. The former considers the N contained in the grain plus stover along with an estimate of N taken up from the soil. It usually considers an annual time frame. The

whole-crop approach considers the N contained in the root-soil complex along with the aboveground N uptake. The whole-crop method is a long-term approach, which deals with N mineralization in relation to N residues returned; if these two are equal the system is at a steady-state condition where the net change in organic N is small. A basic question to answer in designing a N recommendation system is: How close is the soil-crop system to steady-state conditions? (See Meisinger, 1984 for further details.)

Current N recommendation systems differ greatly in local details, but most contain the following general features (see Table 7–4): (i) use of a crop N factor (a combination of the crop N requirement and efficiency term), which considers yield goals, (ii) use of broad-scale soil properties such as soil association and soil drainage class, (iii) use of historical data such as legume N credits or manure credits, (iv) use of soil mineral N content for areas where percolation in small (western USA), (v) occasional use of economic factors such as the cost of N in relation to the price of corn to fine-tune the final N recommendation, and (vi) the general nonuse of an estimate of N mineralization, although there are a few exceptions.

For continuous cereal crops, N fertilizer needs are generally based on yield goals (i.e., crop N removals) as modified by soil NO_3^-–N levels (Table 7–4). These features are characteristic of soil-crop systems near steady-state organic N conditions and may explain why soil N mineralization tests are not in general use. In addition to these nearly steady-state systems, there are also instances of nonsteady-state conditions such as manured sites and systems that oscillate between two soil organic N levels such as legume–cereal crop rotation systems. These nonsteady-state systems are usually accounted for by manure and legume N credits, which are used in virtually every state. Current N recommendation systems can therefore be described as using the long-term, steady-state approach with periodic exceptions for manured and rotated sites.

The most cost-effective N recommendation system will depend heavily on economic considerations, particularly on the cost of N in relation to price of crop product. Current recommendation systems were developed in an era of inexpensive energy, and consequently inexpensive N, and have basically resulted in a long-term, steady-state approximation. Present and future needs will no longer reflect these conditions. Cost-effective N recommendations systems for expensive N will most likely require a more detailed evaluation of each sites' crop N needs, a more accurate and complete evaluation of the soil mineral and organic N status, as well as careful N management (source, timing, and placement) to ensure high N utilization within the soil-crop systems.

B. Response of Crops to Nitrogen

The primary purpose of applying N fertilizer to crops is to increase the yield of dry matter. An adequate supply of N is essential for optimum yields and is usually associated with vigorous vegetative growth and dark green color. Excessive quantities of this element will usually prolong the growth period, retard maturity, and may result in lodging and susceptibility to diseases in certain crops. Crops usually remove from 30 to 70% of the applied N, depending on the crop, yield, and amount of N applied. With good management, uptake efficiency of applied N by corn grain and stover is in the range of 50 to 70% (Stanford, 1973).

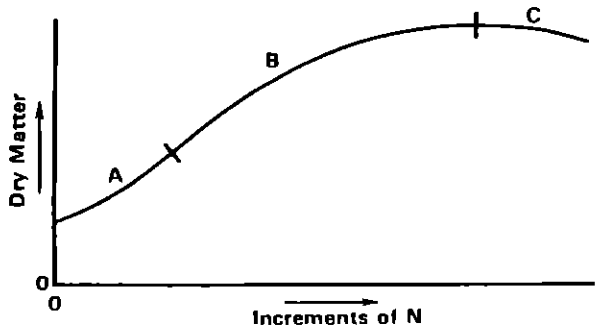


Fig. 7–6. Idealized response in dry matter production of a non-legume to increments of N fertilizer (Viets, 1965).

An ideal N response curve for nonleguminous crops as developed by Viets (1965) shows: (i) a region where succeeding N fertilizer increments produce successively increased yield (Fig. 7–6, segment A), (ii) a region of diminishing returns that contains the most profitable response to applied N (segment B), and (iii) a region of yield depression if excess N leads to lodging or salt damage (segment C). Many factors influence the crops' N response. Some are not subject to management such as drought, certain diseases, or excess soil moisture. Others are manageable in a long-term sense, such as crop rotations, soil drainage, and grass-legume mixtures for forage production. Still others are subject to short-term management such as N sources, rates and methods of application, and the time of application. These latter factors will be discussed in the following sections.

1. Sources of Nitrogen

Most plant roots in soils absorb N as NO_3^- since that form occurs in higher concentrations than NH_4^+ and is free to move to plant roots, primarily by mass flow. Some NH_4^+ is also present and affects plant growth and metabolism to generally unknown degrees (Reisenaur, 1978). Since NH_4^+ is theoretically more efficiently utilized within the plant and is less subject to leaching and denitrification, it should be the preferred source. However, Arnon (1937) and, more recently, Hageman (1980) concluded that, from physiological considerations, either NO_3^- or NH_4^+ can serve as an adequate source of N for plant growth and productivity, but in general NO_3^- salts are considered the "safer" fertilizer. In addition, studies in Wisconsin (Jung et al., 1972; Schrader et al., 1972) and Indiana (Warncke & Barber, 1973) indicated that corn plants prefer a mixture of NH_4^+ and NO_3^- for maximal growth. Schrader et al. (1972) reported that corn plants absorbed NO_3^- and NH_4^+ at equal rates when both forms were present. These field and greenhouse corn trials showed that a combination of these two forms of N enhances uptake of N, growth, and yield.

The relative effectiveness of N sources for crop production will depend on the manner in which they are applied, the chemistry of the soil, and the moisture regime as related to soil textures.

Numerous workers have shown that ammonium sources that form sparingly soluble reaction products with calcium carbonate are inferior when applied to the surface of calcareous soils (Martin & Chapman, 1951; Fenn & Kissel, 1973; Hargrove & Kissel, 1979; Hargrove et al., 1977; Meyer et al., 1961; and Overrein & Moe, 1967) due to NH_3 volatilization (see section V 2). These losses are of major concern in relation to crop production because the use of ammonium sources has increased greatly since the 1950s or 1960s because of their relative low cost of production (Douglas & Cogswell, 1966).

More recently, urea in granular and N solution forms is rapidly becoming the principal N source for agricultural fertilizers (Bridges, 1980). Urea fertilizers have often been inferior to sources such as ammonium nitrate when applied without incorporation. No-tillage management for crop production, which is gaining in popularity because of its potential for soil and water conservation (Phillips et al., 1980), often precludes the easy incorporation of these N sources. Bandel et al. (1980) reported ammonium nitrate was superior to granular or prilled urea and urea–ammonium nitrate solution for no-till corn on acid soils. However, direct measurements of NH_3 losses from these types of system under field conditions have not been reported.

Under conditions of high rainfall, coarse-textured soils, and significant leaching (percolation) potential, NO_3^- sources are usually inferior. However, nitrification is rapid in good agricultural soils when temperature and moisture are optimum; therefore, any advantage for ammonical N is small. Nitrate sources also are inferior due to denitrification under conditions where soils may be waterlogged for periods of time during the growing season. Inferior crop performance in the first case is the result of NO_3^- being physically removed from the system, especially from sandy areas, while in the second case it results from the chemical reduction of NO_3^- to volatile nitrogenous compounds.

Although not addressed in this section, other sources of N for crop utilization may include animal manures, sewage sludge, crop residues, and other organic forms. These considerations of N source will become more important if N costs increase (due to increasing costs of energy) more than unit value of crop output and as greater attention is focused on the possible adverse effects of N on environmental quality.

2. *Rates and Methods of Application*

A basic principle related to rates and methods of N fertilization for optimum crop response is that N be present in sufficient quantities at all times to meet the requirements for plant growth. Too little available N limits production and quality; excess N may lower production, reduce quality, cause lodging, increase disease and insect incidents, and may result in toxic levels in the forage relative to animal consumption. Interactions of the above effects complicate the prediction for the proper N fertilizer application rates. Under certain conditions and in some areas, the soil may supply ample N to meet the needs of the crop.

In recent years, N rates and methods of application for crop production have changed. These changes have occurred because of higher yield levels, increased acreage of irrigated areas for crop production, improved cultivars and genotypes, improved application equipment, and modified management systems such as no-tillage and multiple cropping.

Average N rates for corn have increased markedly over the past 20 yr, from about 45 kg N/ha in 1960 to 125 kg N/ha in 1970 and about 145 kg N/ha in 1980. Novoa and Loomis (1981) pointed out that the demand for N is determined by the growth rate and the N composition of the new tissue. Stanford and Hunter (1973) estimated that an average N content of 1.4% was associated with maximum attainable dry matter yields of wheat grain plus straw. They pointed out the remarkable consistency of that value for several wheat varieties. This value for wheat is higher than that previously reported for corn where the uptake of N per unit of dry matter (grain and stover) associated with maximum attainable yield was essentially constant (1.2%) for a wide range of varieties and growing condition (Stanford, 1973). When Stanford and Hunter projected a wheat grain yield of 3360 kg/ha, they calculated the uptake of N required for attaining yields to be 33 g/kg compared with 21 g/kg for corn.

Different crops respond differently to N; therefore, the most profitable rates vary among crops. Generally, the perennial grasses in the humid and subhumid regions of the USA make the most effective use of N. Corn, as it is grown in the USA, efficiently utilizes N up to the flat portion of the N response curve (last part of segment B of Fig. 7–6). With the possible exception of the new short-strawed wheat and rice varieties, which are less susceptible to lodging than the old varieties, the small grains efficiently utilize less N. Part of this is due to the regions where they are grown, but their genetic potential also is involved. Similarly, the relatively short grasses, such as Kentucky bluegrass (*Poa pratensis* L.), make efficient use of lower rates of N than do the tall, cool-season grasses and such relatively new crops as bermudagrass [*Cynodon dactylon* (L.) Pers.] hybrids. Within plant species, improvements in the yield potential have been made in recent years, which permit higher fertilizer rates than were possible previously. For example, corn has been studied quite extensively to show differences in N response among corn genotypes (Beauchamp et al., 1976; Moll & Kamprath 1977; Pollmer et al., 1979; Moll et al., 1982). At low N supply, differences among hybrids for N use efficiency have been shown to be due largely to variation in internal utilization of accumulated N, while at high N levels differences were due largely to variation in uptake efficiency (Moll et al., 1982). They concluded that in breeding for improved N use efficiency, it would seem desirable for both uptake efficiency and utilization efficiency to be improved simultaneously.

Efficiency in uptake and utilization of N in the production of grain requires that those processes associated with absorption, translocation, assimilation, and redistribution of N operate effectively. One management factor that influences these phenomena is placement and/or method of application. Earlier studies have pointed out the importance of proper place-

ment and mixing of ammonium sources of N with the soil to reduce or prevent NH_3 volatilization (Ernst & Massey, 1960; Gasser, 1964). Overrein and Moe (1967) showed a striking decrease in ammonia volatilization when urea was placed 2.5 cm in the soil. They also showed the decrease to be more rapid with depth and with increasing soil moisture.

In addition to reducing or preventing gaseous losses of N, proper placement is necessary to make the element available to plant roots at the desired time. When band placed, the N should be placed in the proper area so the nutrient can be available quickly to plant roots, yet far enough to avoid seedling damage due to high salt or NH_3 levels (Cummins & Parks, 1961). When N is deficient and N fertilizer is placed near the root system, both root and plant growth are improved due to the banding. In a review, Grunes (1959) showed that N placement often increases the availability of P and other nutrients placed in the same band.

On soils that supply little N and those that are subject to significant N losses by leaching or denitrification, the split-application technique is often employed. When N fertilizer costs are high and commodity prices are relatively low, this practice may be desirable to improve crop utilization efficiency.

In experiments from Nebraska, the grain/stover ratio of corn was 1.4 times greater for sidedressed N than fall or spring applications with the same amount of fertilizer N (Olson et al., 1964). Recently, Thomas (1980) concluded from more than 10 yr of studies in Kentucky that delaying at least half of the applied N fertilizer until 4 to 6 weeks after planting ("knee-high" growth states) resulted in improved efficiency for corn production on soils (i) where drainage is less than perfect, (ii) under no-tillage, and (iii) especially with no-tillage on imperfectly drained soils.

The trend in crop production appears to be toward fewer tillage operations for annual crops. With the concern about energy conservation, siltation of our streams, reduced irrigation water usage, and improved moisture regime, this trend should accelerate. Reducing the amount of tillage might have two effects on N supply from the soil. The first is deeper penetration of water and NO_3^- through larger pores in the wetter, mulched soil. The second effect is cooler soil temperatures, lower evaporation, and slower release of N. These conditions can lead to increased N losses through leaching and denitrification (Thomas et al., 1973, 1981; Unger, 1978). Considering all of these factors, it appears that the N requirement for crops grown with reduced tillage will be somewhat greater than for conventional tillage.

In addition to N losses from the soil-plant system, a significant portion of the N applied in no-till or reduced tillage systems can become immobilized in the decaying residue mulch and, thereby, reduce the amount of N available to the growing crop (Doran, 1980). If N fertilizers are broadcast on top of this decaying mulch, it will likely result in greater immobilization than if N is placed into the soil below the mulch. Good fertilizer management practices (rates and methods of application) will therefore be especially important in no-till systems because of the potential N losses and immobilization.

3. Time of Nitrogen Application

Ensuring the existence of an adequate but not excessive supply of available N for crops during the growing season requires good management relative to time of application and is often related to the particular crop-soil system. For soils with sandy texture, where the indigenous N supply is often low and potentials for N losses by leaching are great, the problem is especially apparent. Increased use of irrigation in recent years has influenced the time of N applications for effectiveness in increasing crop yields. Use of irrigation on sandy soils obviously accentuates possible N loss by leaching. However, certain irrigation management systems may provide a convenient vehicle for multiple application of N, resulting in improved efficiency of this element.

In general, reported research suggests that spring application of N is more effective than fall. Spring application is not always superior, but rarely is inferior to fall applications. Olson et al. (1964) reported that summer side-dressing of fertilizer N for row crops, regardless of chemical form, was usually superior to fall or spring applications. Pearson et al. (1961), working with several soil textures in Alabama, Georgia, and Mississippi, found that N broadcast in November or December was only 49% as effective in increasing corn yields as the corresponding spring application. Fall application of N to corn was < 50% as effective as applied at planting time on two wet soils in western Kentucky (Miller et al., 1975). Jung et al. (1972) found N applied to corn 5 to 8 weeks after planting in Wisconsin was the most effective period of application as shown by increased grain and tissue yield. Nitrogen applied after week 8 showed a distinct reduction in N uptake and yields. In Illinois, fall-applied N was 80 to 90% as effective as spring applications for corn at rates of 67 and 134 kg/ha, but about equally effective at rates of 200 and 268 kg/ha (Welch et al., 1971). Boswell (1971) compared the effects of N plowed down (166 kg/ha) in the fall with winter or spring plowed down N and sidedress N on yields of corn and cotton in Piedmont and Coastal Plain soils of Georgia. No differences in yield were obtained on the heavier Piedmont soil, but on light-textured Coastal Plain soils, yields from N side-dressed in the spring were significantly higher than fall plow-down N.

Timing of N applications for wheat is also important. Hamid (1972) showed that the maximum recovery of fertilizer N in the grain occurred when the N was applied at tillering rather than at earlier or later stages. Earlier work by Olson and Rhodes (1953) indicated similar conclusions. Numerous workers found the relative efficiency of N applied in the fall or winter period was inferior to N applied in the spring near the tillering period (Stanford & Hunter, 1973; Welch et al., 1966; Boswell et al., 1976; Doll, 1962).

Most crops require a continuing supply of N throughout the growing season and this need will vary as to stage of crop maturity. For example, the greatest N uptake period by the corn plant is at 40 to 50% maturity. However, the need for N by the corn plant continues until the corn plant approaches maturity.

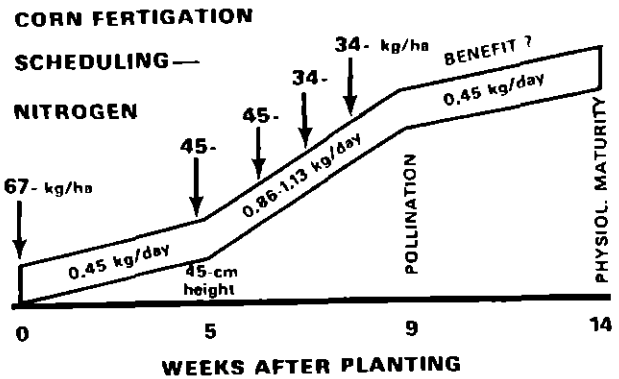


Fig. 7–7. Multiple N fertilization scheme and daily N requirements of corn (Wesley, 1979).

Theoretically, it would be most desirable to add N as closely as possible to the time of maximum uptake by the plant during the growing season. This is especially true if N is applied by fertigation, the practice of applying N through irrigation systems. For example, 225 kg N/ha is recommended for corn yields of 13×10^3 L/ha in Georgia (Wesley, 1979). To increase the N recovery efficiency at this high rate, multiple applications are recommended. If injection equipment is available, four to five applications of N throughout the growing season will increase the N efficiency (Fig. 7–7), based on daily N requirements of corn.

Interest has developed in the timing and splitting of applications of N for forage production. Cool-season grasses normally make a tremendous amount of growth in the spring, and this is stimulated by fertilizing with N. The grass is so efficient in absorbing N that even heavy applications of N in the spring will have a relatively small effect on the growth in the fall. It has been found that two N applications, one early in the spring and one in mid- to late summer, bring about higher yields and better distribution of forage production for grazing. A further subdivision of the first application providing a third application after the first grazing cycle or hay removal further improves the production distribution of the sward.

4. Efficiency of Nitrogen Use by Plants

Response of crops to applied N is an indication of plant efficiency. There are several ways in which efficiency can be considered. The most direct method is to calculate the fertilizer N sorbed by subtracting total N in unfertilized plants from total N in fertilized plants and dividing this value by the N added. Some of the processes affecting efficiency of N use are crop species, soil moisture control, sources of N, rates and time of application, and methods of application. These may, in turn, depend on other factors such as leaching, denitrification, soil N mineralization rate, and past history, which may influence residual N levels.

Grassland has the reputation of being highly efficient in use of N, while efficiencies are relatively low for potatoes (*Solanum tuberosum* L.) and sugarbeets (*Beta vulgaris* L.) (Tinker, 1979). These species may be difficult to compare since, in general, questions of N efficiency revolve around the economically useful parts of the crop. It is quite rare for the amount of N in the roots to be measured; however, if such were practical, estimates of N uptake should therefore be increased. Root functions as related to efficiency may be important where heavy rates of N are necessary for maximum yield.

Pesek et al. (1971) discussed the internal efficiency of plant communities as related to N utilization and pointed out that all individuals of the community of intertilled crops tend to draw on the same environmental resources simultaneously. These efficiencies can be related to plant populations, nature of the root zone as related to moisture, and factors such as sunlight or CO_2 supply.

While a strong effort is made to ensure that plant communities contain only one species of plants, weeds do frequently invade to compete with the crop plants for nutrients and other growth factors. Even modest weed infestations can cause significant reductions in yields with conventional cultivation and no-till systems (Kapusta, 1979; Moomaw & Martin, 1978; Staniforth, 1957). At least part of this competition appears to be for N and other fertilizer elements. Efficiency of N utilization of the crop is, therefore, reduced, and somewhat more N is required to have the same effect on the crop.

5. Legumes as a Source of Nitrogen

Prior to the advent of inexpensive fertilizer N, legumes were often included in rotations to supply N for nonlegume crop production. This practice dates back to ancient times and even early years of the Roman Republic (Pieters & McKee, 1938). Due to increased cost of fertilizer N and diminishing energy resources, renewed interest has developed in legumes as a N source as well as a rotation crop, especially in no-till systems (Ebelhar & Frye, 1981; Mitchell & Teel, 1977; Adams et al., 1970; Hargrove, 1982; Triplett et al., 1979; Touchton et al., 1982). Hairy vetch (*Vicia villosa* Roth) has been reported to supply from 150 to 225 kg N/ha, varying with the amount of top growth. Crimson clover (*Trifolium incarnatum* L.) contains less N than hairy vetch (Mitchell & Teel, 1977). They found that hairy vetch and crimson clover mixtures produced corn grain yields comparable to those obtained by the application of 112 kg N/ha as inorganic fertilizer. They also reported that approximately one-third of the total N from the mulch covers were released to the corn in a single season. The remaining N would be expected to be released at a lower rate during subsequent years.

Although legumes have been utilized over a long period of time to boost N levels for nonlegume plant production, numerous management aspects need additional research. For example, one of the primary problems with winter legumes as a N source is the cost associated with establishment. Development of early maturity species is needed for multiple cropping systems. Information on pest control for the legume and the influence of the legume cover crop on diseases, nematode, and insect damage to subse-

quent crops is not fully understood. Additional studies are needed to develop cropping systems in which legumes, as the N source, may be used most effectively.

VII. CONCLUSIONS

Since 1955, N consumption in the USA has increased almost linearly. The largest total N use increases occurred in the periods of 1965 to 1970 and 1975 to 1980. During the last 5-yr period, N costs have increased appreciably due to current diminishing energy resources. Increasing energy costs have underscored the need for improving N uptake efficiencies.

Areas of high energy requirement as related to N are manufacturing and distributing. Nitrogen fertilizers are highly energy-intensive and require energy both as feedstock (source of H for NH_3) and fuel (including steam). Most of the direct and indirect energy uses in the fertilizer sector depends primarily on nonrenewable hydrocarbons. Despite the high energy input for N fertilizer, the increased energy in crop output is often greater than used for N production.

After the N fertilizer is manufactured, commercial energy is also required for transport preparation, for transportation to the farm level, and for application to the crop. However, the total amount of energy required for distribution and application is rather small relative to its manufacture. The major share of energy required for distribution is in transportation of fertilizer products and raw materials. This transportation is usually by railcars, river barges, trucks, and/or pipelines. The pipeline is currently acting as the long-distance transporter for anhydrous NH_3 and N solutions. Even though this means of transportation is in its infancy, it is expected to increase with usage of these products.

When N sources were available at lower costs, marketing policies were related to production capacity and, through sales and promotion, profits were attained via volume. Current management policies call for the marketing focus to be toward the farm customer's satisfaction and thus attain positive margins through integrated marketing profits.

About 90% of the fertilizer N used in the USA is in the form of ammonia- or ammonium-producing compounds; about 65% of this amount is anhydrous NH_3. The remainder is chiefly accounted for by nitrate, primarily from ammonium nitrate. Improving N fertilizer effectiveness requires an understanding of the factors governing N transformations in soils. Added fertilizer N becomes intimately involved in the soil N cycle, which is composed of many complex biological, physical, and chemical processes. The fertilizer N may be lost from the soil-crop system as a gas or in percolating water, it may be converted to slowly available organic compounds, or it may be taken up by crops. Ammonium fertilizers are subject to substantial NH_3 volatilization losses if they are surface-applied and are in an alkaline environment. Ammonium fertilizers will usually be readily converted to nitrate within several weeks, unless nitrification is retarded due to chemical inhibitors or environmental conditions. During the ensuing weeks the NO_3^-–N may be utilized by plants, denitrified, or leached, but a vigorously growing crop is generally the major sink for fertilizer N during the growing season. Any excess N remaining in the soil beyond the growing season is subject to leaching and/or denitrification losses in humid climates. In dry climates, the excess N will likely remain in the soil as NO_3^-–N.

Soil scientists have studied the behavior of fertilizer N in soils intensively since the 1950s or 1960s to get more fertilizer into the crop. Crop N utilization can be improved through practices such as liming, soil tillage, water management, and crop rotations, but improvements in N uptake efficiency are most readily accomplished through fertilizer management practices such as source, rate, time, and method of application. High N use efficiencies require a combination of all these factors; a given N source should be applied to minimize gaseous losses and immobilization, at a rate that does not exceed the crop assimilation capacity, and at a time in phase with crop demand.

Although much research effort has gone into estimating N uptake efficiencies by the plant, additional studies are needed to investigate factors affecting efficiency to better predict this parameter for specific locations. Such studies require careful definition of the boundaries of the soil-crop system in time and space and also assess the sources of variation that underlie varying N fertilizer needs (e.g., crop differences and soil NO_3^-–N levels).

The most cost-effective N recommendation system will depend heavily on economic consideration, particularly on the cost of N in relation to product price. Current recommendation systems were developed in an era of inexpensive energy, and consequently inexpensive N, and have basically resulted in a long-term, steady-state approximation. Present and future needs will no longer reflect these conditions. Cost-effective N recommendation systems for expensive N will most likely require a more detailed evaluation of each sites' crop N needs, a more accurate and complete evaluation of the soil mineral and organic N status, as well as careful N management (source, timing, and placement) to ensure high N utilization within the soil-crop system.

Even though urea use almost doubled from 1975 to 1980, it is predicted that its use will continue to increase rapidly. Additional information is needed relative to its use and efficiency. With increased costs, it becomes more important to improve uptake efficiency and provide "prescription-type" recommendations for all N fertilizer sources.

Although legumes have been utilized over a long period of time to boost N levels in the soil for nonleguminous plants, numerous management aspects need additional evaluation. Development of cropping systems in which legumes may be used more effectively as N sources still must be studied.

We should continue to be aware of the importance of N fertilizers in producing adequate food of superior quality to feed the growing population of the USA and the world. Biological scientists will have to be sure that N fertilizer is used efficiently and responsibly.

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8

Slow-Release and Bioinhibitor-Amended Nitrogen Fertilizers

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Numerous nitrogen (N) tracer and nontracer studies on crop recovery of applied N indicate that 50 to 60% of fertilizer N added to soil usually is taken up by crop plants during the season of application. The percentage often is lower for flooded rice (*Oryza sativa* L.) or for crops growing in high-rainfall areas. Many of the factors that contribute to incomplete plant recovery of applied N are a result of rapid dissolution of the fertilizer and thereby, release of N at high concentration. These factors affect N movement within and from the plant-soil system, maintenance in plant-available forms, and use by the plant.

One approach to increasing the efficiency of N fertilizer use by plants is to control the rate of N fertilizer dissolution. This can be done by (i) developing compounds with limited water solubility and (ii) modifying water-soluble materials to delay release of their contained N to the soil solution. A second approach is to combine N fertilizers with chemicals that control unwanted N transformations in soil, i.e., developing fertilizers amended with inhibitors of biochemical activity in soil, such as nitrification and urea hydrolysis. Among the reviews on this subject, attention is drawn to those on slow-release N by Army (1963), Hamamoto (1966), Hayase (1967), Hauck and Koshino (1971), Prasad et al. (1971), Hauck (1972), and Allen (1984), and to those on use of nitrification inhibitors by Hauck and Koshino (1971), Prasad et al. (1971), Hauck (1972, 1980), and Slangen and Kerkhoff (1984). These references offer guides to the literature regarding the use of slow-release N and nitrification inhibitors in various cropping systems and their transformations and effects in soils. This chapter focuses on materials that were discussed only briefly or not at all in the earlier reviews and refers to work published before 1970 only where necessary to provide background information or to emphasize an important finding. In this regard, some of the introductory discussion from the author's previous reviews will be repeated.

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Production, Marketing, and Use of Sulfur Products

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The essentiality of S for plant growth has been recognized for approximately 140 yr. Sulfur is a macronutrient, although plants require much less of it than of N or K. The quantities of S required by most crops are comparable with requirements for P or Mg. Deficiencies of S were identified as early as 1900 in the northwestern USA and in 1927 on some soils in Alberta, Canada (Beaton, 1969).

Long before the essentiality of S for plant growth was confirmed, the practical value of applying gypsum was recognized. From 1790 to 1815, much gypsum was imported into the eastern states from mines near Paris (from which the phrase plaster of paris originated). The gypsum was used in conjunction with legumes to enhance the N status of soils (Craven, 1925).

Interest in S as a plant nutrient has increased in recent years. Such interest extends beyond increased crop yields. Food quality, especially low contents of essential S-containing amino acids, is a matter of serious concern in many technologically less-developed areas of the world (Evans et al., 1977). Widespread S deficiency has already been demonstrated in some of these areas (Bromfield, 1972, 1975).

Studies in West Africa suggest that S yields of crops (and thus yields of protein) are restricted by the quantity of S supplied in the rainwater (Bromfield, 1974; Fox et al., 1977). If pollution control measures are effective, atmospheric contributions of S will decrease with time. Thus, there are expectations that decreased atmospheric pollution will lead to even less sulfate (SO_4^{2-}) in rainwater, and this in turn will lead to more intense and expanded S deficiencies than have heretofore been recognized.

Sulfur deficiencies have been demonstrated by field experiments in many sections of the world, including numerous sections of the USA and Canada. These deficiencies seem to be appearing with greater frequency for the following reasons:

1. Increased use of high-analysis fertilizers, which are practically free of S.
2. Greater crop yields with disproportionately greater S utilization.
3. Better control of air pollution, thus decreasing this important source of S.
4. Decreased use of S as a fungicide and insecticide.
5. Improved ability to identify S-deficient soils.
6. Decreased levels of soil organic matter and less dependence on soil organic matter as a source of nutrients.
7. More diligent search for instances of S deficiency by agricultural research workers, representatives of industry, and farmers.

Factors that tend to mitigate against S deficiency are at work also. Among these are decentralization of industry, population shifts from areas of high population density to low density, and the general buildup of population pressure with increased use of manures and fertilizers that do contain S.

Sulfur deficiencies become more numerous and serious when heavy rates of S-free fertilizer are applied. In particular, the need for fertilizing agricultural crops with S is closely related to the amounts of N being applied (Fox, 1976). Figure 11–1 demonstrates the interrelationships between these two nutrients for production of wheat forage and grain in Australia. There was no response to either N or S alone, but growth increased

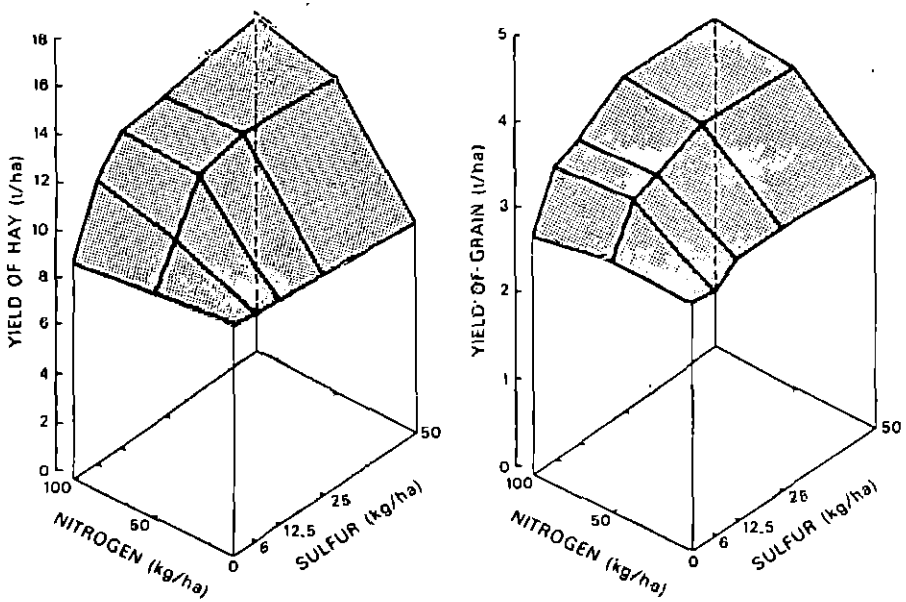

Fig. 11–1. Effect of S and N supply on wheat hay and grain yields (Spencer & Freney, 1980).

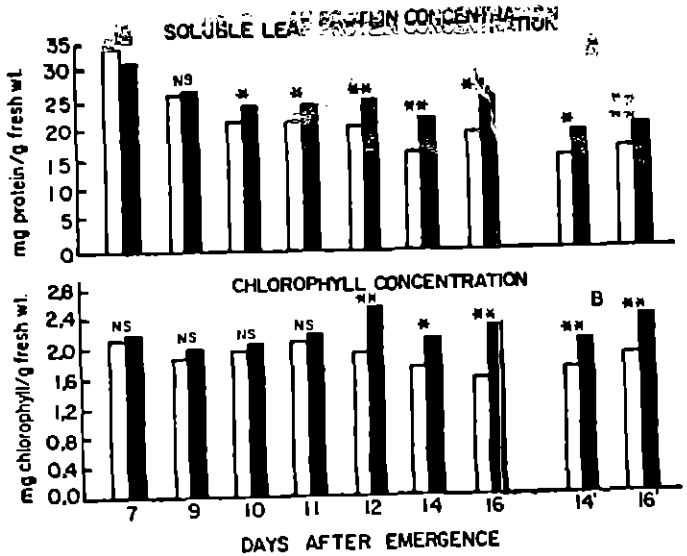

Fig. 11–2. Effect of S deprivation on the concentration of soluble protein and total chlorophyll in leaf blades of S-deprived (□) and normal (■) corn seedlings at various times after emergence. *, ** Significantly different at 0.05 and 0.01 levels of probability, respectively (Friedrich & Schrader, 1978).

substantially when both were applied. The beneficial effect of S increased with the rate of N added.

Inadequate S retards the growth of plants because it is needed for the following essential roles:

1. Component of the amino acids, cystine, cysteine, and methionine, which are required components of proteins.
2. Synthesis of chlorophyll, even though there is no S in this vital plant component. The effect of S deprivation on lowering chlorophyll concentration in leaf blades of corn seedlings is evident in Fig. 11–2.
3. Activation of certain proteolytic enzymes, such as the papainases.
4. Synthesis of certain vitamins (biotin and thiamin or vitamin B_1), glutathione, and coenzyme A.
5. Formation of the glucoside oils of plants such as onion and those in the Cruciferae family.
6. Formation of certain disulfide linkages that are associated with the structural characteristics of protoplasm. (The concentration of sulfhydryl [–HS] groups in tissues of some plants is related to cold and drought resistance.)
7. Formation of a ferredoxin that has an important role in photosynthetic processes (Arnon, 1965; Zaneti & Forti, 1969).
8. Formation of a ferredoxin-like compound that is involved in N_2 fixation by root nodule bacteria (Koch et al., 1970) and free-living N_2-fixing soil bacteria (Bullen, 1968).
9. Activity of ATP sulfurylase, an enzyme concerned with the metabolism of S (Adams & Rinne, 1969; Ellis, 1969).

Table 11-1. Effect of S deprivation on concentration of NO_3-N and on fresh weight of leaf blades and stems of corn seedlings at various times after emergence (Friedrich & Schrader, 1978).

Days after emergence	NO_3-N		Fresh wt	
	No S	Plus S	No S	Plus S
	— mg/kg fresh wt —		— g —	
	Leaf blades			
7	39	27	2.68	2.76
9	38	24	3.36	3.50
10	45	37	4.16	4.02
11	52	34	4.22	4.01
12	32	19	4.44	4.27
14	46	14	4.57	4.66
16	10	23	4.95	5.24
14‡	29	24	4.75	5.00
16‡	23	12	4.78	5.12
Mean§	37**	25**	4.05NS¶	4.07 NS¶
	Stems†			
7	319	224	1.78	1.85
9	378	248	2.34	2.37
10	346	238	2.91	2.80
11	363	356	3.41	3.35
12	360	267	3.84	4.04
14	369	283	4.34	4.97
16	341	350	5.23	5.96
14‡	416	255	4.50	5.26
16‡	418	312	4.91	5.96
Mean§	354**	280**	3.41**	3.62**

** Means significantly different at 0.01 level of probability. Comparison at individual harvest dates are not statistically significant.
† Includes leaf sheaths, unfurled leaves, and culms.
‡ Includes treatments where SO_4^{2-} was added at day 12.
§ Does not include treatments where SO_4^{2-} was added at day 12.
¶ NS = not significant.

10. Activity of nitrate reductase, the enzyme responsible for conversion of nitrate-N (NO_3-N) taken up by plants into amino acids and then into protein. Because of lower activity of this enzyme due to S deficiency, there are reductions in soluble proteins and increases in nitrate (NO_3) concentration in plant tissues (Fig. 11–2 and Table 11–1).

Crops differ in their internal requirements for S, as is evident from the S contents of several crops listed in Table 11–2. High-yielding crops such as sugar crops, Coastal bermudagrass, orchardgrass, corn, and sorghum contain more S than most other crops. A ready supply of S probably is just as important for vegetable crops, rape, and cotton, although the quantity of S taken up by such crops is generally in the intermediate range. Alfalfa, which has been one of the most S-responsive crops, does not accumulate unusually large amounts of S. Most small grains and grasses require less S. Table 11–2 also shows that the S contents of many crops are similar to the contents of P and Mg.

Table 11-2. Approximate quantity of nutrients contained in various crops.

Crop	Yield	N	P†	K‡	S	Mg
	kg/ha§					
	Grains¶					
Corn (*Zea mays* L.)	12 000	343	50	220	47	71
Grain sorghum [*Sorghum bicolor* (L.) Moench]	8 000	288	54	205	43	40
Wheat (*Triticum aestivum* L.)	5 000	156	32	104	23	25
Barley (*Hordeum vulgare* L.)	5 000	156	26	130	26	–
Oats (*Avena sativa* L.)	3 500	109	21	109	21	21
Rice (*Oryza sativa* L.)	7 000	145	24	144	19	16
	Forage crops¶					
Alfalfa (*Medicago sativa* L.)	12 000	359	34	240	33	33
Clovers (*Trifolium* spp.)	8 000	178	20	147	20	26
Bermudagrass 'Coastal' [*Cynodon dactylon* (L.) Pers.]	22 000	629	71	385	49	55
Orchardgrass (*Dactylis glomerata* L.)	16 000	318	49	293	57	–
	Oil crops¶					
Soybeans [*Glycine max* (L.) Merr.]#	3 500	216	26	117	11	14
Peanuts (*Arachis hypogaea* L.)	3 500	256	23	117	29	33
Rapeseed (*Brassica napus* L.)	2 000	90	16	110	35	–
	Fiber crops¶					
Cotton (*Gossypium hirsutum* L.)	1 500	150	40	90	28	19
	Stimulant crops¶					
Tobacco (*Nicotiana tabacum* L.)	3 500	110	13	187	25	28
	Sugar crops					
Sugarcane (*Saccharum officinarum* L.)¶	70 000	141	20	245	84	115
Sugar beets (*Beta vulgaris* L.)††	70 000	187	29	245	57	–
	Vegetables					
Potatoes (*Solanum tuberosum* L.)‡‡	25 000	208	25	266	28	25
Cabbage (*Brassica oleracea* var. *capitata*)§§	45 000	147	16	110	41	11
Turnip (*Brassica rapa*)††	70 000	133	26	222	45	26
Onions (*Allium cepa* L.)¶¶	45 000	135	27	99	28	13

† P × 2.3 = P_2O_5.
‡ K × 1.2 = K_2O.
§ kg/ha × 0.9 = lb/acre.
¶ All aboveground portions.
# Beans only.
†† Tops and roots.
‡‡ Tops and tubers.
§§ Heads.
¶¶ Tops and bulbs.

The data in Table 11–2 implies that internal S requirements of crops are approximately equal to the S contents given but may not be a useful guide for S fertilization. Cotton, a crop that is very sensitive to S deficiency, is among the lowest of the various crops ranked according to S contents. Nevertheless, it is clear that crops cannot produce beyond certain limits imposed by the S supply. Table 11–2 should provide a reasonable estimate of what the minimum external S supply must be.

One other aspect of the S requirement of crops should be introduced because it bears directly on the use of S fertilizers: the concentration of S in the root environment. External S requirements for near-maximum yields have been estimated for several crops. From the results of these investiga-

tions, it seems reasonable to generalize that for many crops this requirement should be approximately 5 mg/L S in solution, but the requirement may be as low as 2 mg/L for some crops (Fox, 1980; Fox et al., 1979). Sulfate in the soil solution is transported to root surfaces in water taken up by plants, a process commonly referred to as *mass flow*.

Sulfur may have beneficial side effects on plant growth in addition to its role as a plant nutrient. The acidifying effects of ammonium thiosulfate, ammonium sulfate, elemental S, and so forth in fertilizer bands in basic or alkaline soils may increase the availability of other essential nutrients, such as P, Mn, and Zn. Large quantities of elemental S or sulfuric acid (H_2SO_4) are usually required for more general pH adjustments. Sulfur and a number of its compounds are useful for reclaiming sodic soils, and many of these same materials are used for treatment of irrigation water to improve water infiltration and percolation.

This topic of production, marketing, and use of S products was reviewed thoroughly by Beaton and Fox (1971). In this chapter we have updated and added new material on the subject.

I. SULFUR SOURCES

A. United States and World Reserves

Sulfur has been known for > 6000 yr, but its widespread use began only about 200 yr ago (Hatch, 1972). As early as 2000 B.C., Egyptians used S to bleach cotton and linen and to formulate various paint pigments and dyes. It was used by the Greeks and Romans as a medicine, a disinfectant, a fumigant, and for religious rites. Sulfur is the "brimstone" of the Bible, and before the time of Christ, the Chinese used S for making gunpowder. The Romans also used it in warfare as an incendiary weapon. Sulfur was popular with the alchemists, and they found it ideal for many of their purposes.

Sulfur constitutes approximately 0.1% of the earth's crust and most commonly occurs as elemental S (brimstone) in deposits associated with calcite, gypsum, and anhydrite; combined S in metal sulfide ores; combined S in mineral sulfates; hydrogen sulfide (H_2S) contaminant in natural gas; organic contaminants in crude oils; pyritic and organic compounds in coal; and organic compounds in tar sands (Comiskey et al., 1969).

World S resources are vast and, for all intents and purposes, unlimited. However, most of them are uneconomical to develop at current prices (Bixby, 1980a). Reserves of conventional S in the USA and elsewhere in the world are compiled in Table 11–3. Values of > 300 million metric tons in the USA and nearly 2800 million metric tons worldwide indicate that conventional reserves will be adequate in the foreseeable future.

In addition to these conventional reserves, about 1100 trillion metric tons of SO_4^{2-} are dissolved in the oceans and deposited on the earth's surface, primarily in the form of gypsum (Hatch, 1972). Sulfur present in coal, oil shale, anhydrite, and gypsum in the USA alone is estimated to be > 33

Table 11–3. Apparent reserves of S from conventional sources in the World (Pearse, 1974).

Area	Petroleum	Natural gas	Native ore	Dome	Sulfide ores	Pyrite	Total
	million metric tons						
USA	30.5	25.4	101.6	101.6	25.4	25.4	309.9
Canada	5.1	172.7	NS†	–	25.4	25.4	228.6
Mexico	5.1	NS	NS	50.8	10.2	5.1	71.1
Central and South America	30.5	NS	101.6	–	50.8	50.8	233.7
Western Europe	NS	25.4	5.1	–	5.1	25.4	61.0
Eastern Europe and USSR	50.8	50.8	152.4	–	152.4	203.2	609.6
Africa	5.1	NS	NS	–	20.3	20.3	45.7
Near East and South Asia	345.5	508.0	203.2	–	5.1	50.8	1112.6
Far East and Southeast Asia	10.2	10.2	50.8	–	20.3	20.3	111.8
Oceania	–	–	NS	–	5.1	5.1	10.2
Total	482.6	792.5	614.7	152.4	320.0	431.8	2794.1

† NS = not significant.

billion metric tons, more than 10 times world conventional reserves (Pearse, 1974). Canada's Athabasca tar sands in northern Alberta are another potentially very large source of S (Vroom, 1972). They are believed to contain at least 4.5 billion metric tons of S as a 4.5 to 5.0% contaminant of the petroleum. United States oil shales contain about 0.75 to 1.0% S by weight (Rieber et al., 1981).

Sensitivity of utilization of the various S reserves to cost/price relationships is demonstrated in Fig. 11–3. This inverted pyramid shows that the size of reserves and cost of production increase from brimstone at the bottom tip to anhydrite and gypsum, coal, and seawater in the broad upper levels. Normally, if lower cost sources are unable to satisfy demand, the

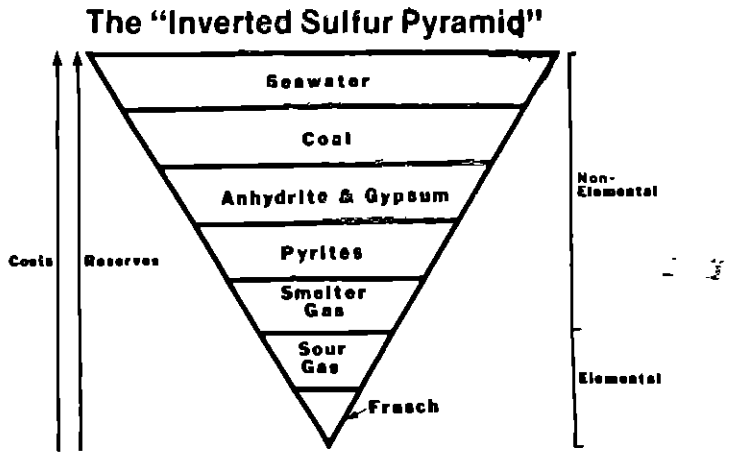

Fig. 11–3. The inverted S pyramid (Bixby, 1980a).

resulting rise in prices makes it economically attractive to develop more expensive sources higher up in the pyramid. A possible exception to this natural relationship might be S from sources where the production costs are subsidized in pollution abatement facilities (Bixby, 1980a).

Sulfur is produced by more diverse and ingenious methods than any other common element (Hatch, 1972). It is dug from pits like coal, recovered from waste gases of smelters (as sulfur dioxide [SO_2]), extracted from natural and refinery gases (as H_2S), and melted underground and brought to the surface as liquid elemental S (the Frasch process). Frasch S is the most important single source of S in the USA (Rieber et al., 1981), but its importance is expected to begin a gradual decline over the next several years until the deposits are depleted or uneconomical to mine (Bixby, 1980a). Forecasts of the amounts of S to be provided from the various U.S. sources in 1985 and 1990 are shown in Table 11–4.

Table 11–4. Estimated U.S. S supply outlook by region and source, 1985 and 1990 (Rieber et al., 1981).

Source	1985	1990
	million metric tons	
Northeast		
Refinery S	0.71	0.91
Recovered acid	0.10	0.20
Total	0.81	1.11
Southeast		
Recovered acid	0.30	0.41
Gulf Coast		
Frasch	4.10	3.56
Refinery S	1.73	2.34
Sour gas S	1.62	2.03
Total	7.45	7.93
Midwest		
Refinery S	0.51	0.71
Recovered acid	0.20	0.30
Coal gas–flue gas	0.20	0.20
Total	0.91	1.21
Midcontinent†		
Frasch	3.05	3.05
Refinery S	0.20	0.30
Sour gas S	1.93	4.57
Recovered acid	1.22	1.63
Total	6.40	9.55
West Coast		
Refinery S	0.61	0.81
Recovered acid	nil	nil
Total	0.61	0.81
U.S. total	16.46	21.03

† Including southwest and intermountain USA.

B. Energy Requirements

Because of the present dominant position of Frasch S in the USA and since more information is readily available about energy consumed in its production, this discussion focuses on this method of S mining. Production costs and energy usage are closely related to the amounts of superheated water at a temperature of 160 to 163° C that must be forced under a pressure of 8.78 to 14.06 kg/cm^2 down a borehole into the underlying S-bearing formation (Ellison, 1971; Pearse, 1974). The quantities of water needed range from about 5600 to 26 000 L/metric ton of S depending on the characteristics of the deposit and the age of the mine (Ellison, 1971).

Energy requirements range from about 4.8 to 9.5 × 10^9 J/metric ton of elemental S (Rieber et al., 1981). It averages about 9.3 × 10^9 J/metric ton of S (Blouin & Davis, 1975). Most of this is heat energy, generally from natural gas.

According to Blouin and Davis (1975), S recovery from sour gas requires only about 0.35 × 10^9 J/metric ton of S. Desulfurization of oil is energy intensive, consuming approximately 31.4 × 10^9 J/metric ton of S. Production of S from the roasting of pyrites utilizes almost 0.5 × 10^9 J/metric ton, just slightly more than that used in sour gas recovery.

II. SULFUR FERTILIZERS

Many fertilizer materials contain significant quantities of S. Brief descriptions of the most popular S sources are listed in Table 11–5.

A. Fertilizers Containing Elemental Sulfur

1. Agricultural, Flake, and Porous Sulfur Granules

The use of elemental S to reduce soil pH and to reclaim sodic soils is well known. However, problems of dustiness, unpleasantness, and hazards of fire and explosion have limited the utility of agricultural grade S and to a lesser extent the flake form for fertilizer purposes. Modifications are possible to overcome these serious drawbacks and at the same time take advantage of the obvious economics in using practically pure S. Unfortunately, these changes, which mostly entail larger or more durable particles, are usually made at the expense of agronomic effectiveness.

Pure S is easily prilled, but the product is unsuitable for normal fertilizer uses because it is virtually insoluble and has low surface area. These properties seriously delay the rate at which it will be converted to plant available SO_4^{2-}. One way of improving the effectiveness of prilled elemental S is to form porous irregular granules with much greater surface areas. This is the approach taken with products such as Popcorn Sulfur (Unocal Company of California, Los Angeles, CA) and Poro-Sul (Smith and Ardussi, Inc., Seattle, WA) The performance of flake S can, of course, be controlled to some degree by changing flake size and thickness.

Table 11-5. Sulfur-containing fertilizer materials (Bixby & Kilmer, 1975).

Sulfur as S	Sulfur as SO_4^{2-}
Agricultural S	Ammonium sulfate
Flake S	Potassium sulfate
Granular S-bentonite	Calcium sulfate
Phosphate rock–S	Magnesium sulfate
Normal superphosphate + S	Potassium–magnesium sulfate
Triple superphosphate + S	Normal and enriched superphosphate
DAP† + MAP‡ + S	Ammonium nitrate–sulfate
Ammonium polyphosphate + S	Ammonium sulfate–nitrate
AP-UP§ + S	Ammonium phosphate–sulfate
NPK grades + S	Ammonium phosphate–sulfate gypsum
Urea-S	Ammonium phosphate–sulfate urea
Potash-urea-S	Several micronutrient salts
S-coated potash	Urea-sulfate
S-coated urea	Urea-ammonium sulfate
Ammonia-S	Sulfuric acid
S suspensions	NPKS
Micronutrients in S	
Sulfur in other forms	
Ammonium thiosulfate	
Ammonium bisulfite	
Ammonium polysulfide	
Sulfur dioxide	
Certain ultra-high analysis materials	
Lime-S	

† DAP = diammonium phosphate.
‡ MAP = monoammonium phosphate.
§ AP-UP = ammonium phosphate–urea phosphate.

Flake S and the porous S products are used for direct application and bulk blending. These sources are probably incapable of correcting S deficiencies during the first growing season after application unless approximately 25% of the particles are < 60-mesh size. On severely S-deficient soils and ones of low or unknown S oxidizing capacity, these products should be used in conjunction with some soluble SO_4^{2-}. Also, under these kinds of conditions they should be applied and incorporated into the soil as far in advance of seeding as possible.

2. Water-degradeable Granular Sulfur-Bentonite

Another means of improving the effectiveness of granular elemental S products is to incorporate 5 to 10% by weight of a swelling clay such as bentonite. This fertilizer imbibes soil moisture and disintegrates into finely divided S, which is more readily converted to SO_4^{2-}. One manufacturing procedure involves cooling the molten S-bentonite mixture on stainless steel slating belts, followed by crushing and screening. A product with similar constituents but formed by prilling is currently being evaluated.

Granular water-degradeable S-bentonite fertilizers are manufactured at several locations in the USA and Canada. Agri-Sul (Agri-Sul Inc., Mineola, TX), Degra-Sul (Degra-Sul Fertilizer Production Ltd., Calgary, Alberta), Disintegrating Flake (Montana Sulphur and Chemical Co., Billings, MT), Disper-Sul (Chemical Enterprises, Inc., Houston, TX), Terasul (Canadyne Chemical, Burlington, Ontario), and Tiger 90 (Tiger Chemical Ltd., Calgary, Alberta) are commercial examples. They are used for both direct application and blending with other compatible dry sources of N, P, and K. Some of these products are dusty, especially when they are subjected to rough and excessive handling with augers. A surfactant may be sprayed on the granules to reduce dusting and provide wettability.

Because of uncertain effectiveness of these S sources during the first growing season after fertilization, the same provisions should be made that were outlined for agricultural, flake, and porous S materials. Repeated use of elemental S-containing fertilizers tends to gradually enlarge the population of S-oxidizing microorganisms, resulting in a corresponding increase in the rate of SO_4^{2-} formation.

3. Sulfur Suspensions

Elemental S can be readily used in suspensions. The Tennessee Valley Authority (TVA) has used −20-mesh, crushed lump S to make suspensions containing 60% S and 1% clay. Complete formulas, such as 9–8–15–10S (9–18–18–10S) and 12–5–10–20S (12–12–12–20S), have been prepared from 12–18–0 (12–40–0), urea–ammonium nitrate (UAN) solutions, potassium chloride (KCl), and S.

One commercial firm has successfully made and applied a 60% S slurry. A portable mixer suitable for field use and equipped with a motor-driven impeller was used to make the slurry, which was then pumped to field applicators and sprayed onto the soil using existing liquid fertilizer equipment. The S slurry can also serve as a carrier for micronutrients.

Another company provides instructions on how to formulate a 52% S suspension from −100-mesh S and either 1% predispersed liquid clay or 2% regular clay. Surfactant at a rate of 1% and a mixing time of 3 min are also called for in the formulation.

Relatively inexpensive, crude elemental lump S reduced to the desired size by suspension equipment has not proved entirely satisfactory. Dry ground S is more efficient but has obvious drawbacks. Evaluations are being made of an alternate source of S provided from ground S-bentonite products or fines from their manufacturing processes. This material is less dusty than flowers of S, yet it has a sufficiently fine particle size to give a good short-term suspension.

Although more costly, S suspensions intended for fungicidal purposes can be diverted to fertilizer uses. One product of this type is a cream-yellow liquid containing 40 to 54% S, with a particle size of only 1 to 2 μm.

4. Phosphate-Sulfur

Monoammonium and diammonium phosphates containing from about 5 to 20% S can be made by applying a hydraulic spray of elemental S at 1.4 kg/cm² during drum or pan granulation. At TVA, a product containing 12% N, 23% P, and 15% S (12–52–0–15S) was prepared by spraying

liquid S onto a rolling bed of granular ammonium polyphosphate. On the basis of limited experience with these materials, it appears that they are excellent sources of both P and S (Beaton et al., 1968–1969). They should be satisfactory for bulk blending with other granular fertilizers or for direct application, particularly for topdressing legumes when both P and S are required.

A granular concentrated superphosphate-S fertilizer with an analysis of 0–18–0–20S (0–40–0–20S) was produced experimentally at TVA. The process involved granulating elemental S and concentrated superphosphate with the aid of steam and water in a drum granulator. A similar material analyzing 0–15–0–28S (0–35–0–28S) was made for a short time in the western USA. In spite of enthusiastic acceptance, production was terminated because of fire and explosion hazards connected with the grinding of oversized granules. If there were sufficient economic incentive, this product would likely be manufactured again, but in an inert atmosphere.

Sulfur fortification of normal superphosphate is popular in Australia and New Zealand. In Australia these specially prepared high S fertilizers are supplied in two grades—S.F. 25 and S.F. 45, with the numerals indicating total S concentration (Bell, 1975). They are manufactured by metering liquid S into the acidulation mixer. These materials are homogeneous, containing both SO_4^{2-} for fast release and from 18 to 37% elemental S for longer-term release in soils where leaching losses of SO_4^{2-} are serious. The two S-fortified superphosphates commonly produced in New Zealand contain 10 and 20% elemental S and provide one-half and one-third, respectively, of the total S as SO_4^{2-} (Muller et al., 1975).

There has been periodic activity and interest, dating back to at least 1916, in the preparation of phosphate rock–S mixtures. Evaluation of their agronomic effectiveness is incomplete. Biosuper (Australian Mineral Development Lab., Frewville, S. Australia), a granular phosphate rock–S product containing thiobacilli has been under investigation in Australia since the mid- to late 1960s. This material contains about 16% S, and the preferred ratio of phosphate rock to S is 5:1 (Swaby, 1975).

As a result of the activity of the thiobacilli, sulfuric acid is formed, which partially reacts with the phosphate rock to form superphosphate. Thiobacilli do not form spores, and death of the inoculum by dehydration during storage of Biosuper is a problem. The surviving thiobacilli will, however, accelerate S oxidation and formation of soluble P, particularly in soils deficient in native S-oxidizing organisms. Biosuper seems to be well suited for topdressing pastures in tropical areas of Australia and other countries where the annual precipitation exceeds 635 mm.

5. Urea-Sulfur

The complete miscibility of urea and liquid S facilitates production of a homogeneous granular product with excellent storage and handling properties. A 40–0–0–10S prilled material was manufactured and marketed on a limited scale in the mid-1960s in the western USA. Although all other properties were favorable, its S component had limited availability for early growing season response.

TVA prepared a granular urea-S analyzing about 44–0–0–4S by spraying molten S and urea melt as separate streams into a pilot plant pan granulator. The desired fineness of S particles was achieved by atomization.

In the early 1980s, a drum granulated urea-S became commercially available in western Canada. This homogeneous fertilizer material has a typical analysis of 36–0–0–20S. It has superb storage and handling characteristics. As might be expected due to differences in population and activity of S-oxidizing organisms at the experimental sites, field results have been variable, but in general they show that the S component becomes available in a reasonable period of time.

6. Sulfur Coatings

One way of achieving controlled release of soluble forms of plant nutrients is to coat them with relatively insoluble and affordable materials such as elemental S. TVA first made S-coated urea (SCU) in laboratory and bench-scale tests conducted about 1961. This controlled-release N fertilizer as currently produced is 77 to 82% urea and 14 to 18% S coating. At least three firms manufacture SCU products—one each in the USA, Canada, and the U.K. Sulfur used in these protective coatings will become available for plant uptake.

At TVA, S coatings for controlled release purposes have also been successfully applied to urea–ammonium phosphate granules and granular KCl.

Sulfur coatings may also be used to intentionally supply plant nutrient S. For example, a product analyzing 40–0–0–10S made by coating urea with finely divided S using oil and calcium lignosulfonate as a binder is being used on rice and Coastal bermudagrass in the west south central states, in Mississippi, and in Mexico.

7. Other Fertilizers Combined with Elemental Sulfur

A few other fertilizer products of only minor importance have been made by adding elemental S in one way or another (e.g., anhydrous ammonia–S and micronutrient-S fusions).

B. Fertilizers Containing Sulfate

Sulfate-containing fertilizers provide most of the fertilizer S applied to soils. These materials have the advantage of supplying S in a form that is immediately available for plant uptake. In areas with high leaching losses of plant nutrients, fast-acting sulfates may not be as effective as sources containing elemental S, which slowly convert to SO_4^{2-}.

1. Ammonium Sulfate

Ammonium sulfate is one of the oldest of the N- and S-containing fertilizers, and it still remains popular. In 1975 to 1976, it accounted for ap-

proximately 5.2 million metric tons of plant nutrient S worldwide (Bixby & Kilmer, 1975). Approximately 58% of it is synthetic, 16% is a by-product from metallurgical operations, and 26% is a coproduct from manufacture of caprolactam, the raw material for nylon 6, a synthetic fiber.

The popularity of ammonium sulfate (21–0–0–24S) has been due largely to its competitive price as a source of N. Part of its production cost is frequently charged against the primary product from which it results. At times there is virtually no charge for the S values in ammonium sulfate, but this is changing because of the increasing attention being given to plant nutrient S.

The uses of ammonium sulfate as a solid fertilizer are well known. It is applied alone or blended with other fertilizer materials. Segregation problems can occur in bulk blends when its product size is not well matched with those of N, P, and K materials. This difficulty can be minimized by carefully controlling uniformity and sizing of ammonium sulfate used in blends.

When ammonium sulfate is used for direct application as a N source, much more S is applied incidentally than is required by most crops. In addition to this N/S imbalance, excessive soil acidity can develop when frequent high rates are applied to poorly buffered soils.

Ammonium sulfate can supply up to 10% S in suspensions. When it is used in suspension blends high in K, S concentrations of only about 1 to 2% are possible.

It can also be used in clear liquids. For certain local situations involving short hauling distances and low costs for product, ammonium sulfate is used to make solutions analyzing about 8% N and 9% S. Sulfur concentrations in solutions based on ammonium sulfate and UAN solution can vary from 1 to 9%. An example of this combination is a 25–0–0–3.5S solution sold in the eastern USA. In NPS blends formulated with ammonium sulfate, the usual S concentrations range from 1 to 3%.

2. Ammonium Nitrate–Sulfate

Ammonium nitrate–sulfate with a grade of 30–0–0–06.5S is manufactured in Washington State. It is made by granulating a slurry of the double salt. At TVA, similar products analyzing 30–0–0–5S and 27–0–0–11S were made by neutralizing nitric acid (HNO_3) and sulfuric acid (H_2SO_4) with ammonia, and concentrating and feeding the product onto a tumbling bed of recycled product on a pan granulator.

A double salt of ammonium nitrate and ammonium sulfate present in equal proportions was formerly produced as a synthetic product in the Federal Republic of Germany. It was known as Leunasalpeter and had a grade of 26–0–0–13S. This S source has several advantages, including less hygroscopicity, a satisfactory N/S ratio for direct application purposes, and a combination of ammoniacal and nitrate forms of N, making it suitable for both spring and fall fertilization. In the U.S. Pacific Northwest, ammonium nitrate–sulfate is widely used on forage and grass seed crops and on fall-seeded small grains.

3. Urea–Ammonium Sulfate

For a few years beginning in 1976 a granular urea–ammonium sulfate fertilizer with a grade of 40–0–0–6S was commercially produced in western Canada. It was made by coating ammonium sulfate fines with urea in a spherodizing drum. Although this S source was replaced by a new urea–elemental S material, which was mentioned previously, a second manufacturer began production in 1984 of a similar material analyzing 38–0–0–7S.

Granular urea–ammonium sulfate has been made by a variety of ways at TVA. Grades ranging from 40–0–0–14S to 30–0–0–13S have been produced by oil prilling. It was also made by coating ammonium sulfate fines with urea in a granulator and by air prilling.

Urea–ammonium sulfate granules tend to be more resistant to physical breakdown and less hygroscopic than urea prills. Its physical properties can be further improved by the addition of gypsum, which forms a complex with urea. The N/S ratio may be varied from 3:1 to 7:1, resulting in considerable flexibility in the correction of N and S deficiencies in most soils. Uses in the western USA were similar to those described earlier for ammonium nitrate–sulfate.

Mechanical mixtures of urea and ammonium sulfate with a grade of 34–0–0–11S have been sold in western Canada since 1967, and they are still well accepted. Because of segregation problems caused by unsatisfactory product sizing of ammonium sulfate, which were mentioned earlier, these blends should be used soon after they are prepared and not stored in fertilizer dealers' bins or on farms. Also, the amount of handling should be minimized.

TVA has demonstrated the feasibility of producing a 29–0–0–5S urea–ammonium sulfate suspension. It is made by reacting anhydrous ammonia, H_2SO_4, 75% urea solution, and water in a tank-type boiling reactor (National Fertilizer Development Center, 1980). Two cooling stages are used, and 2% attapulgite gelling clay is added during the first cooling stage. Handling and storage properties are good, and the N/S ratio of nearly 6:1 is favorable. This product may be used either for direct application or as a base suspension in the manufacture of suspension mixtures by a simple cold-mixing procedure.

4. Ammonium Phosphate–Sulfate

The most common grade of ammonium phosphate–sulfate analyzes 16–9–0–14S (16–20–0–14S). It is composed of about 40% monoammonium phosphate and 60% ammonium sulfate. Other products of this type include 13–16–0–20S (13–39–0–20S), 19–4–0–20S (19–9–0–20S), and 23–9–0–7S (23–20–0–7S). The latter contains some urea.

They are made by several processes, including reacting a mixture of phosphoric acid (H_3PO_4) and sulfuric acid with ammonia, and introducing ammonium sulfate solutions and H_2SO_4 into a H_3PO_4 plant reaction circuit.

Direct application of 16–9–20–14S (16–20–0–14S) to forage crops, particularly legumes, is practiced in many areas. It is also popular for in-row applications on small grains and rapeseed/canola seeded on previously fallowed land. This product is frequently used for formulating bulk blends.

A granular product with a grade of 15–13–0–8S (15–30–0–8S) is currently manufactured in the southeastern USA. Ammonium phosphate, ammonium sulfate, and gypsum are used to make this product, which is suitable for both bulk blending and direct application.

5. Gypsum

Gypsum ($CaSO_4 \cdot 2H_2O$) is used as a source of S in the localities where it is mined or produced as a by-product. Its low nutrient analysis, 13 to 19% S, limits the extent to which it can be profitably used. Although finely divided gypsum is difficult to apply, two U.S. manufacturers now make an easily spreadable granular form. Gypsum has the added benefit of supplying Ca for either plant nutrient or soil amendment purposes.

There is a vast supply of this mineral from mines situated in several parts of the USA and Canada. Appreciable quantities are also produced as a by-product in the manufacture of wet-process H_3PO_4.

6. Normal Superphosphate

Normal superphosphate was at one time a major source of P and still is prominent in Australasia due to its 10 to 14% S content. Normal superphosphate is composed of approximately 50% by weight each of monocalcium phosphate and gypsum or its lower hydrate. The occurrence of S deficiencies has been delayed in many areas of the world because of the involuntary addition of S when normal superphosphate was used to supply P. Its Ca content, ranging from 18 to 21%, can be important in soils low in this nutrient.

7. Potassium Sulfate and Potassium–Magnesium Sulfate

Potassium sulfate analyzing 0–0–42–17S (0–0–50–17S) and potassium–magnesium sulfate with a grade of 0–0–18–22S (0–0–22–22S) plus 11% Mg are important sources of S. They are particularly useful when low levels of chloride are desired, as is often the case for crops such as tobacco, potatoes, avocado (*Persea americana* Mill.), peach [*Prunus persica* (L.) Batsch], some legumes and turf grass. These two products also supply K, S, or Mg individually or remedy multiple deficiencies of these elements.

Both materials are suitable for direct application, bulk blending, and inclusion in suspensions. Potassium sulfate is least abrasive of the two products. The abrasion problem with potassium–magnesium sulfate has been largely overcome in a modified product that is ground to −20-mesh size and then regranulated.

8. Magnesium Sulfate and Sulfates of Micronutrients

Magnesium sulfate containing 13% S and 9.8% Mg has limited use as a source of Mg in clear liquid fertilizers and foliar sprays (Beaton & Bixby, 1973). Significant amounts of S will also be provided when it is used to supply Mg.

Micronutrient sulfate salts are also incidental carriers of S. For example, in the group consisting of Cu, Fe, Mn, and Zn, concentration of S varies between 13 and 21%.

9. Sulfuric Acid and Urea–Sulfuric Acid

Use of sulfuric acid (H_2SO_4) as a soil amendment is discussed later. The usual concentration of acid used for this purpose is 93%, and it contains about 30% S. Thus, there will be substantial additions of S when arid lands are treated with H_2SO_4.

Personal hazards have restricted the use of H_2SO_4. A simple, rapid, and economic process has been developed in California to combine urea and H_2SO_4 into a product with greatly reduced destructivity of human tissue without neutralizing any of the acidity of the sulfuric acid (Gregory, 1983). A mild skin irritation may occur after prolonged exposure to this product, and it will sting on contact with a cut or sore on the skin.

The reaction between urea and concentrated H_2SO_4 is strongly exothermic, and measures must be taken to dissipate the heat evolved in the process (Verdegaal & Verdegaal, 1982). The resulting end product is a liquid that remains in the fluid state to temperatures of −2.2 to 3.3° C, depending on the formulation. Urea–H_2SO_4 fertilizers have a pH of < 1, and stainless steel and thermoplastics such as polyethylene, polyvinyl chloride, polyvinylidene fluoride, and polypropylene must be used for manufacturing, storing, and handling them. Workers must use rubber protection equipment, especially footgear.

Typical urea–H_2SO_4 formulations, amendments, and fertilizers have grades of 10–0–0–18S, 15–0–0–16S, and 28–0–0–9S. Urea–Sulfuric acid fertilizers can be applied in any manner that conventional fertilizers are applied, provided that suitable corrosion resistant equipment is used. They can be broadcast before planting or shanked in as a sidedressing. In addition, they can be applied in surface irrigation water or injected into circle pivots, linear moving systems, and drip systems. Other fertilizer materials such as 10–15–0 (10–34–0) and H_3PO_4 are compatible with urea–H_2SO_4 fertilizers.

C. Fertilizers Containing Other Forms of Sulfur

Two materials containing reduced or partially oxidized S compounds are commonly used in the rapidly expanding market for fluid fertilizers. These are ammonium thiosulfate and ammonium polysulfide. Use of ammonium bisulfite, a once popular S source in certain localized areas of the Pacific Northwest, has diminished in recent years and became almost nil in 1982. Sulfur dioxide is a high-analysis liquid that is not used for soil applications because of technical difficulties, but it is commonly used for water treatment in California and Arizona.

1. Ammonium Thiosulfate

Ammonium thiosulfate solution, 12–0–0–26S, is the most widely used S product in clear liquid fertilizers. It is prepared by reaction of SO_2 and aqueous ammonia, followed by further reaction with elemental S. Several variations of this basic process exist.

This material is compatible in any proportion with neutral to slightly acidic (not < pH = 5.8) orthophosphate and polyphosphates. It can also be readily blended with aqueous ammonia and with UAN solutions. It is not suitable for mixing with anhydrous ammonia.

The versatility of ammonium thiosulfate is such that it can be used to provide up to 10 to 12% S in a wide variety of N–S, N–P–S, and N–P–K–S formulations. Trial blends should be prepared, especially when K is a component, before going to large-scale mixing.

It is essentially noncorrosive and may be stored in mild steel and aluminum containers. However, contact with tin, copper, brass, or other copper alloys should be avoided. Storage temperatures of between −1 and 38° C are permissible.

Ammonium thiosulfate is well adapted to the many methods of applying fertilizer solutions, and it can be applied through open ditch and sprinkler irrigation systems. It has favorable soil amendment properties also, but there are less expensive alternatives.

2. Ammonium Polysulfide and Calcium Polysulfide

Ammonium polysulfide is a highly alkaline (pH 10) reddish brown solution with a strong odor of hydrogen sulfide (H_2S). It analyzes 20–0–0–45S and is made by reacting aqua ammonia with H_2S and elemental S in the presence of heat and agitation.

Ammonium polysulfide is compatible with anhydrous ammonia, and at volumes > 10% it is stable in both aqua ammonia and urea–ammonium nitrate solutions. Blending with acidic solutions should be avoided because it will decompose in them, releasing H_2S and colloidal S. Generally, it is considered unsuitable for mixing with phosphate solutions, although there are exceptions. Complete N–P–K–S solutions containing up to almost 6% K are possible with this product as a component.

Storage and handling equipment should be made of black iron, stainless steel, aluminum, or certain poly-type plastics. Brass and bronze metal parts are subject to severe corrosion. It can be stored at temperatures ranging from −1 to 38° C. This product should be stored at a pressure of 0.035 kg/cm^2 to prevent loss of ammonia and subsequent precipitation of S.

It may be applied directly in open ditch irrigation systems, but addition through sprinkler systems is not recommended. This material in mixtures of aqua ammonia or anhydrous ammonia is injected into soil using anhydrous ammonia applicators. It can be applied directly to the soil surface if diluted with water to lower the N concentration to < 5%. Urea–ammonium polysulfide solution, 25–0–0–35S, is applied in irrigation runs to many crops in the southwestern USA. At one time in this region of the USA, a blend of ammonium polysulfide and anhydrous ammonia analyzing 55–0–0–20S was specially formulated for soil injection.

Although ammonium polysulfide is an excellent source of plant nutrient S, its primary uses are as a soil amendment and for water treatment. It is not as convenient or as pleasant to handle as is ammonium thiosulfate. For example, after equipment is used for handling and distributing ammonium polysulfide, it must be thoroughly cleansed with water or anhydrous ammonia.

A 29% solution of calcium polysulfide is used similarly to ammonium polysulfide as a soil amendment and for water treatment. It contains 22% S and 7% Ca, has a pH of 11 to 12, and has a strong odor of H_2S. The amendment action of 100 kg of calcium polysulfide is equivalent to 147 kg of 100% gypsum or 27.6 kg of elemental S.

Calcium polysulfide may be applied at rates of 120 to 600 kg/ha through flood or furrow irrigation systems. Higher amounts may be used under certain conditions. When calcium polysulfide is applied to growing crops, rates in a single application should not exceed 120 to 180 kg/ha.

3. Ammonium Bisulfite

Ammonium bisulfite, a low analysis (8.5–0–0–17S) solution with a strong odor of sulfur dioxide, was once an important source of S in a localized region of the Pacific Northwest. This material is well suited to mixing with aqueous ammonia and urea–ammonium nitrate solutions. Similar to ammonium polysulfide, it should not be mixed with acidic solutions. In most other respects it is used in the same ways as ammonium thiosulfate.

Mild steel, aluminum, and plastic tanks are suitable for storing ammonium bisulfite.

4. Sulfur Dioxide

Liquid SO_2 contains 50% S and for a time was considered a potentially useful high analysis S fertilizer. It is kept under pressure and for this reason has to be applied with anhydrous ammonia injection equipment. One of its major disadvantages is incompatibility with anhydrous ammonia, necessitating a separate tank and pump on application rigs.

Despite its lack of acceptance for fertilizer purposes, SO_2 is used as a soil amendment and for water treatment. It is produced from elemental S in specially designed field burners for addition to irrigation waters in Arizona and California. More is said about this aspect of its use in section VI regarding S soil amendments.

For more technological and agronomic information on the use of the principal S fertilizers, the recommendation tables drawn up by Bixby and Beaton (1970) and Beaton and Fox (1971) are useful. Considerable detail on mixing techniques for supplying S in liquids and suspensions is given in reviews by Beaton and Bixby (1973) and Bixby (1978). A comprehensive list of S fertilizer materials along with producers and suppliers was compiled by Bixby (1980b).

III. MARKETING SULFUR FERTILIZERS

Need for fertilizer S in the USA and Canada has grown considerably in recent years. In 1960, S deficiencies had been confirmed in field experiments in 13 states, and by the early 1980s, this number had increased to 35. Five provinces in Canada now have recognized shortages of this nutrient.

A. Consumption in the United States and Canada

Despite the widespread occurrences of S deficiencies in the USA and Canada, use of fertilizer S is far below crop requirements. Approximately 1 million metric tons of S were applied in the USA in 1972–1973 compared with calculated crop requirements ranging between 2.3 and 3.6 million metric tons of S (Beaton et al., 1974). Although both usage and crop needs of S are expected to be somewhat greater now, the gap between them has probably not narrowed. It should be recognized that not all of this fertilizer S consumption was planned; much of it was applied incidentally as a component of N–P–K fertilizer materials.

Crop responses to fertilizer S are common in the four western Canadian provinces of British Columbia, Alberta, Saskatchewan, and Manitoba. Annual additions of fertilizer S in these four provinces during the 11 yr from 1969 to 1979 ranged between 18 800 and 44 000 metric tons (Beaton, 1980). The 39 600 metric tons applied in 1979 are considerably lower than the estimated 0.15 to 0.2 million metric tons needed for the seven main crops grown in the three Prairie Provinces. Very little of this S use was deliberate, but rather it was incidental mainly in the form of popular materials such as ammonium sulfate, ammonium phosphate–sulfate, ammonium phosphates, and the various 1:1 and 2:1 nitrogen phosphates based on ammonium phosphate.

These deficits between crop requirements for S and the amounts applied in fertilizer are probably not as large as indicated. In some regions of the USA and Canada, there are undoubtedly substantial S contributions in wet and dry deposition from the atmosphere and in irrigation waters. Sulfates in irrigation water are often more than adequate for crop requirements.

B. Market Development

Market development for S is carried out by many fertilizer manufacturers in individual programs and by their support of research and education organizations such as the Sulphur Institute and the Sulphur Development Institute of Canada. Other organizations aiding in collective development programs are the Potash & Phosphate Institute and its affiliated Foundation for Agronomic Research. These industry-financed institutes are staffed with highly qualified scientists that serve the fertilizer industry, universities, government, and agriculture in the USA, Canada, and elsewhere in the world.

The industry-sponsored organizations document the need for S for sound use in crop and livestock production. They fund research projects at universities and other research establishments to develop this kind of information and to obtain basic knowledge about S in soils, plants, and animals. Assistance is also given to demonstrations of the need for and benefits from using S in agriculture.

Strong educational programs are a major part of the market development activities of the industry-supported organizations. There is extensive use of publications such as the *Sulphur Institute Journal* (now restructured and renamed *Sulphur in Agriculture*), technical bulletins, newsletters, and leaflets. Visual aids, including 35-mm color slides and color films are also important educational tools. All of these items are designed to inform agricultural leaders among growers; in research, extension and instruction; bankers; and agribusiness of significant findings on the role of S in profitable crop and livestock production. Timely press releases on this same topic are sent to various farm publications.

Staff of the Sulphur Institute and to a lesser extent the Potash & Phosphate Institute frequently make presentations on S-related topics at farm meetings, crop production seminars, fertilizer dealer meetings, fertilizer association conferences, and at meetings of professional associations. These organizations periodically hold symposia, workshops, and other educational meetings to assemble researchers, educators, administrators, and members of industry to report on and evaluate problems and progress made in S research. Specific S-related topics may also be reviewed and discussed at these meetings.

In addition to research grants offered to universities and other domestic research agencies, some financial and technical assistance is given to international agencies such as the United Nation's Food and Agriculture Organization's fertilizer program.

Company-identified market development activities may take a number of directions. The principal ones are in-house research and development projects; exhibits at trade shows and other meetings of the various state, regional, and national fertilizer associations; and provision of funding and materials for research projects at universities and government research agencies. Other approaches used are direct mailers on S-related topics to farmers and agriculturists and advertisements in farm newspapers and magazines, on radio, and perhaps on television.

In some cases, qualified fertilizer company personnel prepare technical literature, write educational articles for farm publications, and give talks on subjects on various aspects of S in crop and livestock production.

C. Marketing Programs

Sulfur fertilizer manufacturers market their products in different ways depending on how the individual firm is structured. Producers who have company-owned or franchised retail dealerships (or both) will sell S-containing materials through these outlets. Manufacturers with and without such retailing capability may also sell to wholesale distributors, who in

turn will service retailers. Several manufacturers of special S-containing materials do not have any retailing facilities. They market directly to dealers, and substantial quantities may also be handled through wholesalers. Rarely are S fertilizer products sold directly from the manufacturer to the grower.

By purchasing S fertilizers through retail outlets, farmers have access to both local and broader expertise on the use of and benefits from applying S. They will also be able to have fertilizer S, where required, blended with common N–P–K materials.

D. Marketing Problems

One serious complication in the marketing of fertilizer S is the existence of large supplies of by-product ammonium sulfate. The low monetary value often credited to the S component of ammonium sulfate makes it difficult for other more costly S-containing products to be price competitive.

There have been marketing problems with several of the elemental S-containing sources. Brief accounts of these difficulties are given in the discussions on concentrated superphosphate-S and water-degradeable granular S-bentonite materials in section IIA2. More serious consequences of the dust problem resulting in destruction of a manufacturing plant in Alberta in early 1980 were reported by Beaton (1980).

IV. FORMS OF SULFUR IN SOILS AND THEIR UTILIZATION BY PLANTS

Soils contain both inorganic and organic S. As far as we know, plants utilize the inorganic SO_4^{2-} form of S almost exclusively. This is not to imply that organic forms of S are unimportant; many soils of the humid and subhumid temperate zone contain very small quantities of inorganic S. In such soils plants quickly utilize (or percolating waters readily leach from the root zone) S mineralized through the slow and continuous oxidation of soil organic matter, together with S that accrues as dissolved SO_2 in rainwater and SO_2 absorbed directly by soils from the atmosphere.

Even though the immediate source of S for plants is inorganic SO_4^{2-}, organic S is the original source for most of the SO_4^{2-} used by plants. Because of this, organic S has been referred to as *reserve S* (Bardsley & Lancaster, 1960), a term generally appropriate for soils that contain relatively little inorganic S in relation to organic S.

Some soils contain so much SO_4^{2-} in relation to organic S that the term reserve S seems inappropriate to describe the organic fraction. Two cases serve as examples: gypsum-rich soils of arid and semiarid regions and soils developed in highly weathered volcanic ash materials with very high capacities to sorb SO_4^{2-}. Such are the Andepts of Hawaii, which may contain as much as 0.7% SO_4^{2-}-S in the soil material below 30 cm (Hasan et al., 1970).

Sulfate-sulfur is present in soils in three forms: in solution, as a precipitate, and adsorbed onto colloid surfaces. Gypsum is the most frequently

encountered precipitate of SO_4^{2-} in soils. It is a sparingly soluble salt (ca. 450 μg S/mL in water). The concentration of SO_4^{2-} in equilibrium with solid phase gypsum dihydrate is several times greater than the level plants require for good nutrition.

Most highly weathered soils contain sorbed SO_4^{2-}, some of which contain great quantities, whereas soils with properties dominated by the layer-silicate clay minerals (they contain little of the hydrated oxides of Fe or Al) sorb little SO_4^{2-}. For example, 58% of readily extractable S in a group of soils from Brazil was sorbed SO_4^{2-}, but only 2% in soils from Iowa was sorbed SO_4^{2-} (Neptune et al., 1975). Some uncertainty exists about the nature and availability of this SO_4^{2-}. It is usually thought to be retained on sesquioxide surfaces by some kind of ligand exchange mechanism. Adams and Rawajfih (1977), however, have demonstrated that basaluminite and alunite could be the cause of SO_4^{2-} retention by acid soils.

The concentration of SO_4^{2-} in soil solutions is highly variable, especially in soils that have little capacity to sorb SO_4^{2-}. Such soils are relatively unbuffered against depletion of SO_4^{2-} by plant uptake and leaching or against accumulations resulting from organic S mineralization, fertilizer applications, or moisture depletion. A determination of the apparent solubility of SO_4^{2-} in profile samples of 11 soils from Puerto Rico, all with an appreciable capacity to sorb SO_4^{2-}, gave a range of 0.4 to 24 μg/mL (Fox, 1982).

If soils have an appreciable capacity to sorb SO_4^{2-}, the concentration of SO_4^{2-} in solution will depend to a great degree on the percentage saturation of the sorption complex with SO_4^{2-}.

Data collected on soil profile samples primarily from highly weathered soils of Hawaii (Hasan et al., 1970) and Puerto Rico (Fox, 1982) suggest that if soils are to have 5 μg/mL of SO_4^{2-} in solution, the SO_4^{2-} sorption capacity should be, on average, 60 to 80% saturated. Not much SO_4^{2-} is required to attain this for most surface soil materials, because the SO_4^{2-} sorption capacity is usually relatively low for the surface horizon. This is demonstrated for an Ultisol of Puerto Rico in Table 11–6. Note that 0.6 μg S/mL in solution, probably a deficient condition, was associated with 10 mg S/kg of soil and a SO_4^{2-} saturation percentage of only 20.

Table 11–6. Status of SO_4^{2-}-S in selected depth increments of Daguey soil† from Puerto Rico (Fox, 1980).

Depth increment	Sorbed SO_4^{2-}	SO_4^{2-} in solution	SO_4^{2-} sorption maximum	SO_4^{2-} saturation
cm	mg S/kg	μg S/mL	mg S/kg	%
0–10	10	0.6	51	20
10–30	170	3.0	435	39
30–60	250	1.5	548	46
60–95	373	1.5	671	56

† Clayey, oxidic, isohyperthermic Orthoxic Tropohumult.

V. REACTIONS OF SULFUR FERTILIZERS IN SOILS

Many factors influence the efficiency of S fertilizers. In very general terms, the effects these factors have on fertilizer efficiency will depend on the kind of fertilizer materials involved, the nature of the soil, crops used, weather conditions, and time.

A. Elemental Sulfur

Because SO_4^{2-} is the form of S taken up by plants, S in lower oxidation states must be oxidized before it is used. Elemental S is converted to SO_4^{2-} by biological oxidation. Although autotrophic and heterotropic bacteria, fungi, and actinomycetes are capable of oxidizing elemental S, the autotrophic thiobacilli are the most important. Some soils are underpopulated with S-oxidizing organisms. When elemental S is added to such soils, some time will elapse while the microbial population builds up. Elemental S oxidation is affected by particle size. The relationship between surface area of the S particles and S uptake by corn growing in a S-deficient soil was almost perfectly linear (Fig. 11–4).

Temperatures between 30 and 40° C and soil moisture contents higher than field capacity favor elemental S oxidation. Oxidation proceeds most rapidly when the elemental S is mixed with the soil. If elemental S is banded in acid sandy soils, adding lime in the band will speed oxidation (Table 11–7).

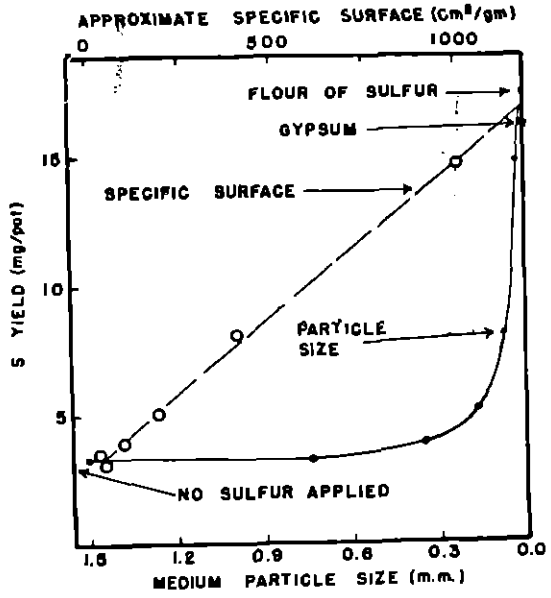

Fig. 11–4. Sulfur yield in corn plants 32 d after planting in relation to the specific surface of S particles. The rate of S addition was 5 mg/kg in all treatments (Fox et al., 1964).

Table 11–7. Sulfur yield in corn plants 28 days after planting as influenced by placement of different S-containing [illegible]

S treatment	S yield, Unlimed	S yield, Limed
	mg/pot	
	Fertilizer mixed	
None	4.3	3.3
Gypsum	14.1	–
S flour	16.6	14.7
	Fertilizer banded	
Gypsum	15.4	–
S flour	8.4	14.3

B. Other Forms of Sulfur

Thiosulfate, sulfites, and sulfur dioxide are converted chemically and biologically to SO_4^{2-}. Because these materials are usually applied to the soil in fluid form, a high degree of contact with the soil is expected. Several of these materials undergo transformations, resulting in the formation of colloidal S when they are added to soil. Thiosulfates are chemically unstable in acid solution, yielding SO_2 and elemental S. The polysulfides are chemically unstable and form colloidal S and sulfides when added to soil. These soluble sulfides rapidly oxidize chemically to elemental S. Oxidation of elemental S formed from these fluid products probably proceeds biologically and is influenced by temperature and moisture in the same way as elemental S applied directly to soils. Particle size of the elemental S formed during these transformations is believed to be ideal for subsequent oxidation.

Sulfur dioxide reacts with water in the soil to form sulfurous acid, which in turn reacts with soil constituents to form sulfite salts. These oxidize to SO_4^{2-} either chemically or biologically.

C. Sulfates

Regardless of the form of S fertilizer applied to soils, the end product in well-aerated soils is SO_4^{2-}. The SO_4^{2-} will form sparingly soluble salts with cations such as Ca^{2+} in the soil. Sulfates coprecipitated with $CaCO_3$ in soils probably are relatively unavailable to plants. In humid regions, SO_4^{2-} usually leaches into the subsoil where it may accumulate; however, soluble SO_4^{2-} salts frequently leach through the profile below the root zone. Sulfate is less mobile in soils than NO_3^- and Cl^- and is less subject to leaching losses. This is one reason why the fertilizer requirements for S tend to be less than would be expected relative to N.

Many highly weathered soils have a considerable capacity to adsorb SO_4^{2-}. Sulfate sorption by soils is concentration dependent. Fertilizers that greatly increase SO_4^{2-} concentration in the soil enhance SO_4^{2-} sorption. The reaction is reversible. Plants can utilize adsorbed SO_4^{2-}. Although the rela-

tionships are far from perfect, evidence suggests that the availability of adsorbed SO_4^{2-} is only slightly less than soluble SO_4^{2-} or at least is in keeping with its solubility in the soil system (Barrow, 1969; Fox, 1980; Hasan et al., 1970; Hogg & Toxopeus, 1966). Adsorption of SO_4^{2-} should help to conserve S fertilizers and native soil S by reducing leaching losses and regulating the movement of SO_4^{2-} to the roots of plants. Liming and phosphate fertilization reduce the capacity of soils to sorb SO_4^{2-}. The short-term effect of these practices may be increased availability of fertilizer or soil sulfates because of increased SO_4^{2-} solubility. The long-term effects are likely to be increased depletion of S in surface horizons because of greater leaching.

Sulfate in strongly anaerobic soils may be reduced by bacteria to form H_2S, which in turn reacts with heavy metals to produce highly insoluble sulfides. If the system later becomes oxidized, these sulfides oxidize to elemental S, which is converted by biological oxidation to sulfuric acid, causing very acidic conditions.

VI. PREDICTING AND DIAGNOSING THE NEED FOR SULFUR FERTILIZERS

A. Available Soil Test Levels

Efforts to develop S soil tests have been largely concentrated on measuring SO_4^{2-} as an estimate of available S (Ensminger & Freney, 1966). Some recommended extraction solutions have been (i) monocalcium orthophosphate [$Ca(H_2PO_4)_2$] or monopotassium orthophosphate (KH_2PO_4), (ii) neutral salt solutions, (iii) hot water, (iv) sodium acetate (NaOAc, pH 4.8), and (v) sodium bicarbonate ($NaHCO_3$). The first two measure soluble plus some adsorbed SO_4^{2-}, and the remaining procedures also include some organic S. Solutions containing phosphate have given the highest correlations of extractable S related to crop yields or S uptake by plants. In pot tests, correlation coefficients *(r)* of 0.8 and 0.9 have been reported (Barrow, 1967; Scott, 1981), but in the field an *r* of 0.4 is more usual (Hoeft et al., 1973; Probert & Jones, 1977).

Some workers have found no significant relationships of soil test values to crop yields or S uptake in the field (Spencer & Glendinning, 1980). Soil tests appear to be of most value on sandy soils. For example, Reneau and Hawkins (1980) observed a response to S in Virginia on corn and soybeans grown on Coastal Plain soils. These are moderately well to well-drained soils, low in organic matter, belong to the fine loamy or coarse-textured families, and have $Ca(H_2PO_4)_2$–extractable soil S concentrations of 6 to 7 kg S/ha or lower. Soils with the same soil characteristics but with soil S concentrations between 7 and 15 kg/ha would be expected to respond to applications in dry years but not in wet years. This response appears to be related to soil moisture conditions and the depth and concentrations of extractable S in subsurface horizons.

Brogan and Murphy (1980) in Ireland reported that soil testing for S was not promising. They observed, however, that soils with > 55% sand and < 3% organic C were likely to respond to S.

B. Plant Analysis

Four criteria of assaying the S status of plants have been most widely used: (i) total S, (ii) SO_4^{2-}-S, (iii) N/S ratios, and (iv) SO_4^{2-}-S/total S ratio.

Total S is an obvious choice since concentrations are directly related to S supply. However, critical values are affected by plant part sampled, stage of growth, and amount of defoliation previous to sampling, as in the case of a grazed or mowed pasture crop (Jones et al., 1981; Ensminger & Freney, 1966).

Sulfate-sulfur critical values do not change as much as total S with the above variables and critical N/S, and SO_4^{2-}-S/total S ratios change even less. However, the latter two methods require two analyses that increase the cost and the variability. The disadvantages of these four criteria are that time of sampling is restricted to a relatively short period, they indicate only the S status of the plants at the time of sampling, and then only if other nutrient or environmental factors are not more limiting than S. Plant analysis can be useful if time of sampling, plant part, and chemical analysis are properly chosen.

To put the S status in perspective with respect to other nutrients, the diagnosis and recommendation integrated system (DRIS) has been suggested (Sumner, 1981). This appears to have merit where a large data base for yields and chemical composition can be obtained on such crops as corn, soybeans, and alfalfa. However, on pasture crops, yield data from thousands of sites are more difficult and expensive to obtain and are not yet available.

C. Contributions from Atmospheric Sources and Irrigation Waters

Global emissions of S resulting from industrial activities are estimated at 100 to 170 million metric tons annually (Husar et al., 1977). More than 26 million metric tons of SO_2 (13 million metric tons of S) were estimated to have been emitted into the atmosphere of the USA in 1980. Total annual emissions of sulfur oxides in Canada are approximately 7 million metric tons or 3.5 million metric tons of S (Canada Dep. of the Environment, 1978; Summers & Whelpdale, 1975).

Sulfur enters the atmosphere as SO_2, H_2S, H_2SO_4, various sulfate compounds, and as volatile organic compounds such as dimethyl sulfide, dimethyl disulfide, and methyl mercaptan. In unpolluted air, S occurs primarily in three compounds: SO_4^{2-} in aerosols and SO_2 and H_2S gases (Tabatabai & La Flen, 1976). Hydrogen sulfide in the air is normally oxidized to SO_2, which in turn is oxidized to SO_3. Sulfur trioxide dissolves in water droplets to form H_2SO_4, which may react further to form SO_4^{2-} salts such as $(NH_4)_2SO_4$ or $CaSO_4$.

Sulfuric acid and the SO_4^{2-} salts present in aerosols are removed by precipitation and, to a lesser extent, gravitational settling. Sulfur dioxide that enters the air has a residence time of only about 5 days to 2 weeks before it is removed by these mechanisms (Tabatabai & La Flen, 1976).

The most important processes that remove pollutants from the atmosphere (Overrein, 1977) are:

1. Removal by precipitation of gases and aerosols.
2. Absorption of gases by vegetation, soil, and water.
3. Impaction of particles on vegetation and ground.

The first of these processes is called *wet deposition* and the other two *dry deposition*.

1. Wet Deposition

Atmospheric deposition of S in North America generally increases from west to east as it is moved by prevailing winds across the North American continent. In 1980 some areas of Idaho, Nevada, and Utah received < 0.5 kg S/ha whereas the southern Great Lakes and Ohio Valley received 12.5 kg S/ha. (Fig. 11–5). There are smaller areas on the downwind side of industrial complexes where the deposition of S is much higher than the maximum shown.

Amounts of S deposited annually in precipitation in Alberta and Minnesota ranged from 2.2 to 220 kg/ha (Hoeft et al., 1972). They found at 20 locations in Wisconsin from 1969 to 1971 that average annual S in precipitation measured 2 km from an industrial site was 168 kg/ha, whereas at 9 urban and 13 rural sites it was 42 and 16 kg/ha, respectively. The annual addition of S by precipitation at six sites in Iowa varied from 13 kg/ha in northeastern parts of the state to 17 kg/ha in north central Iowa (Tabatabai & La Flen, 1976). These values for Iowa are comparable with those reported for rural Wisconsin.

The wet deposition figures above for Iowa and Wisconsin plus values reported in a number of other states are listed in Table 11–8, which was summarized by Terman (1978). In states bordering the Gulf and southern Atlantic coasts at points not affected appreciably by local industry, the quantities of S in precipitation were usually < 6 kg of S/ha per year. Greater amounts ranging from 10 to 30 kg/ha per year were recorded near local industries and generally over northern Alabama, Kentucky, Tennessee, and Virginia.

An average yearly rainwater return of 28 kg of S/ha has been reported in Ontario along the northeastern shore of Lake Ontario (Rutherford, 1967). In adjoining U.S. states, the amounts of S in rainfall ranged from 9 kg of S/ha in northern Michigan (Cressman & Davis, 1962) to 55 kg of S/ha in New York (Leland, 1952).

In spite of the estimated 0.275 million metric tons of S, primarily in the form of SO_2, emitted yearly to the atmosphere in Alberta, there is surprisingly low washout of only about 1.4 kg of S/ha per year (Table 11–9). Rain falling in remote unpopulated areas of Alberta is characterized by very low

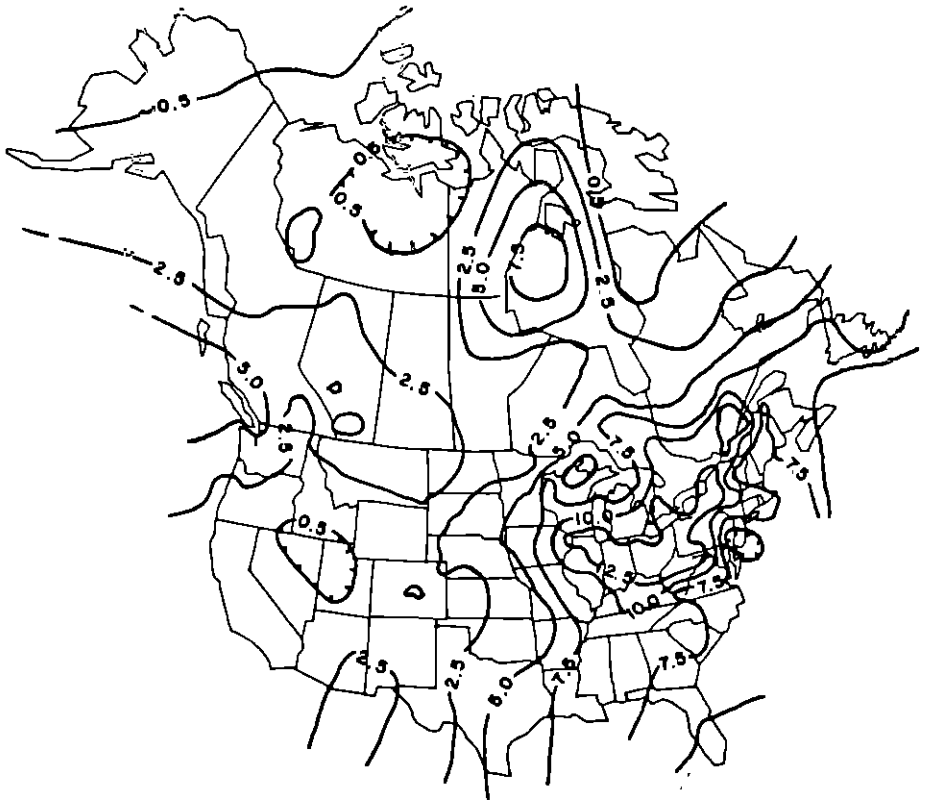

Fig. 11–5. Sulfur deposition isopleth map in kilograms per hectare for January–December 1980 (J. H. Gibson and C. V. Baker, unpublished data, Natural Resource Ecology Laboratory, Colorado State Univ., Fort Collins).

SO_4^{2-}-S content, typically 0.2 mg/L. This level approximates that found in fresh snow and is representative of the global background level of SO_4^{2-}-S resulting from natural sources. Median values for 1973 and 1974 precipitation in central Alberta were 0.7 and 0.5 mg/L, respectively. The annual average SO_4^{2-}-S concentrations in Iowa precipitation, supposedly uninfluenced by industrial emissions, were much higher ranging from 1.08 to 2.31 mg/L.

Sulfur content of precipitation in the tropics is frequently low, as exemplified by a mean value of 1.14 kg/ha per year detected during the rainy season in northern Nigeria (Bromfield, 1974).

From this brief review and many other reports in the literature, it seems that rain and snow usually contain small amounts of S in regions remote from industry, as little as 1 or 2 kg of S/ha per year. Near urban and industrial areas precipitation may contain from 20 to > 100 kg of S/ha per year. Ten kilograms of S/ha per year in precipitation have been used as a rough guide for delineating areas of potential S deficiency.

Table 11-8. Amounts of S found in precipitation in various U.S. states (Terman, 1978).

State	Location in state	No. of sites	Years	Major source	Amounts/yr Range	Amounts/yr Avg
			Southern states		kg S/ha	
Alabama	Prattville	1	1954–1955	General	3.4- 4.0	3.7
	Muscle Shoals	19	1954	General	3.1- 6.8	5.4
	Muscle Shoals	20	1955	Steam Plant	6.4–16.2	11.9
	Muscle Shoals	23	1956	Steam Plant	6.5–16.6	11.0
Arkansas	NW and SE	2	1954–1955	General	2.6- 5.3	3.7
Florida	Cantonment	1	1953–1955	Industry	14.8–52.6	33.5
	Gainesville	1	1953–1955	Urban	8.0- 9.6	8.8
	Others	5	1953–1955	General	1.8- 4.4	3.2
Georgia	Various	6	1954–1955	General	2.8–13.9	7.7
Kentucky	Various	6	1954–1955	General	4.1–22.3	13.1
Louisiana	Various	5	1954–1955	General	2.1–13.9	9.0
Mississippi	Various	7	1953–1955	General	0.8–10.1	5.0
North Carolina	Statesville	1	1953–1955	Industry	12.7–19.4	15.5
	Others	15	1953–1955	General	3.1–14.6	6.0
	Clyde	1	1969–1973	Industry	10.6–43.3	22.1
Oklahoma	Stillwater	1	1927–1942	General	6.9–14.2	9.7
South Carolina	Various	4	1953–1955	General	3.1–17.7	7.5
Tennessee	Various	7	1955	General	10.5–21.4	14.2
	Various	5	1971–1972	General	13.9–20.0	17.1
Texas	Beaumont	1	1954–1955	Industry	10.0–14.1	12.1
	Others	4	1954–1955	General	3.1- 7.5	5.7
Virginia	Norfolk	1	1954–1955	Industry	33.4–37.0	35.2
	Others	14	1954	General	8.4–26.9	15.0
	Others	17	1955	General	13.3–34.5	21.2
	Various	16	1953–1956	General	14.2–37.5	21.4
			Northern states			
Indiana	Gary	1	1946–1947	Industry	–	142.2
	Others	10	1946–1947	General	22.4–37.0	30.0
Michigan	Various	5	1959–1960	Industry	9.0–14.0	11.3
Minnesota	St. Paul	1	1962–1967	Urban and Industry	–	16.5
	Others	3	1962–1967	Urban and Industry	4.1–10.1	7.7
Nebraska	Various	7	1953–1954	General	2.6–15.9	7.2
New York	Ithaca	1	1931–1949	Urban and Industry	34.7–76.2	54.9
Wisconsin	Industrial site	1	1969–1971	Industry	–	168.0
	Urban	9	1969–1971	Urban	–	42.0
	Rural	13	1969–1971	General	–	16.0

Table 11-9. Total yearly average SO_4^{2-}-S deposition in central Alberta, Canada (Klemm, 1977).

Source of deposition	kg SO_4^{2-}-S/ha
Snow (1 November–13 February)	0.45
Rain (June–August)	0.90
Dry fallout (May–November)	0.78
Total	2.13

2. *Dry Deposition*

a. Lead Peroxide Absorption—Lead peroxide (PbO_2) cylinders protected from rainfall have been commonly used to measure the quantity of SO_2 that could be absorbed from the atmosphere. Terman (1978) reviewed this subject, and most of his information is summarized in Table 11–10. Absorption of about 10 kg of S/ha per year or less appeared to be characteristic of rural areas unaffected by urban and industrial activities. Quantities in the 40 to 60 kg/ha per year range were associated with urban centers, whereas amounts of > 300 kg/ha per year were indicative of emissions from industrial point sources.

b. Soil Absorption—Emissions of SO_2 can be directly absorbed by soils, and in some areas such as Alberta it may be the most important mechanism of SO_2 deposition (Nyborg & Walker, 1977). Absorption of SO_2 by bare and cropped soils at two locations in Alberta varied between 20 and 38 kg of S/ha per year. The data in Table 11–9 are supportive since it can be seen that dry deposition was equal in importance to rainout. In a 6-yr study in Sweden exposing potted bare soil, under protective canopies, positioned at distances of 1 to 7 km downwind from a SO_2 source, the ratios of S absorbed directly from the air by soils exceeded that in precipitation by factors of 7 to 2 (Johansson, 1959).

Direct absorption of SO_2 from the air by soils and measurement of subsequent acidification is an indirect method for monitoring SO_2 emissions. This approach is useful but can be misleading because (i) there can be natural fluctuations and variability in soil pH under field conditions, (ii) there can be different buffering capacities in soil, (iii) precipitation affected by S emissions is not always acidic due to formation of neutral SO_4^{2-} salts, and (iv) environmental factors such as soil temperature and moisture will affect the processes of ammonification and nitrification, which tend to dominate soil pH in the short term.

Table 11-10. Amounts of atmospheric SO_2 absorbed by PbO_2 cylinders (Terman, 1978).

State	Location in state (no. of locations)	Years	Major source	Amounts of S, kg/ha per year Range	Amounts of S, kg/ha per year Avg
Alabama	Muscle Shoals (7)	1956	Power Plant	6–30	14
Minnesota	Minneapolis	1937	Urban and industry		460
	Rural site		General		3
	Duluth	1962–1967	General		11
	St. Paul		Urban and industry		41
	Rural sites (2)				7
Virginia	Norfolk	1955	Urban and industry		61
	Others (15)		General	14–39	23
Wisconsin	Alma	1969–1971	Industrial point source		380
	Urban (9)		General		28
	Rural (13)		General		14

c. Plant Absorption—Atmospheric SO_2 can reach plants directly by entering leaf stomata or by being absorbed in moisture on leaves. In either case, SO_3^{2-}-S and then SO_4^{2-}-S are soon formed. Low doses of SO_2 may be harmless or even beneficial. Excessive uptake of SO_2 by vegetation will, however, cause increasingly severe damage, varying from reversible to irreversible. Different degrees of injury may occur on sensitive species upon exposure to SO_2 concentrations above about 0.2 to 0.5 μL/L for 1 h.

Cotton plants well nourished with S in solution cultures still absorbed about 30% of their S from the atmosphere (Olsen, 1957). When S deficient, these plants absorbed up to 90% of their S from air containing 0.01 to 0.05 μL/L of SO_2. However, absorption of SO_2 from the air did not completely satisfy their S requirements. Oats and rapeseed grown in soil treated with ^{35}S-labeled fertilizer absorbed about 50% of their S directly from the air at low S supply but much less at high S supply (Siman & Jansson, 1976).

Faller (1970–1971) demonstrated that tobacco, sunflower (*Helianthus annuus* L.), and corn grown in nutrient solution with S in very low concentration responded to increasing SO_2 concentrations in controlled atmospheres up to 0.525, 0.35, and 0.175 μL/L, respectively. In later trials, Faller (1971) showed that tobacco plants were able to utilize atmospheric SO_2 as the only source of plant nutrient S and that this gaseous form was fully equivalent to SO_4^{2-} supplied through roots.

The large contributions that atmospheric S can make to the total S content of cotton and tall fescue (*Festuca arundinacea* Schreb.) are apparent in Table 11–11. Cotton at the Colbert site and in sand, both very deficient in S, obtained from 84 to 98% of its S requirement by absorption of SO_2 from the atmosphere. Fescue and cotton acted as sinks for atmospheric S when the S supply in the growth medium was low in relation to

Table 11–11. Vegetative production, S content, and source of plant S for cotton and fescue grown at four sites located at varying distances from coal-fired plants in Alabama (Noggle & Jones, 1979).

Growth site	Oven-dry wt	S conc	Total S	Source of plant S		Proportion of plant S from atmosphere
				Soil	Atmosphere	
	g	%	mg		mg/100 g, dry wt	%
Cotton						
Crossville	117	0.12	152	152	0	0
Widows Creek	154	0.19	332	139	193	125	58
Colbert (soil)	356	0.28	1018	139	854	240	84
Colbert (sand)	186	0.25	494	9	485	260	98
Greenhouse	160	0.18	294	129	164	102	56
Fescue						
Crossville	42	0.13	57	57	0	0	0
Widows Creek	60	0.19	115	76	39	65	34
Colbert (soil)	50	0.17	86	57	29	58	34
Colbert (sand)	44	0.18	81	8	73	165	90
Greenhouse	14	0.14	21	13	8	57	38

shelf species. From 75 to 90% of the total S accumulation from the atmosphere was in the form of SO_2.

Terman (1978) suggested that up to half of global plant losses for S could be absorbed as SO_2. Dry deposition of atmospheric SO_2 can be an important source of S, particularly when plant roots are inadequately supplied with SO_4^{2-} but apparently not unless there is an active source close at hand. Bromfield (1974) measured only minor quantities of S as dry deposition in northern Nigeria.

3. Irrigation Waters

Sulfur in waters used for irrigation varies widely, depending on geologic formations and other input sources contributing to the waters. For example, the upper Yakima River in Washington State contributes only 0.7 mg/L and crops respond to S fertilization, but below the Yakima River the water contributes 1.4 mg/L and irrigated crops do not respond to S. At the mouth of the Yakima River the water contains 5.1 mg/L (Dow, 1976). Water from the Colorado River and many wells is also high in SO_4^{2-}.

In California, streams flowing out of the granite formations of the Sierra Nevada Mountains are generally low, ranging from 0.4 to 4.4 mg/L. Streams from the Coastal Range are higher, ranging from 1.6 in the north to 138 mg/L in the south (Martin, 1958).

Generally, irrigation waters carrying more than 4 to 6 mg/L of S will supply enough S for most crops. The applicability of this guideline will of course depend on the interaction of several factors, including (i) the amount of water applied per growing season, (ii) crop requirements, and (iii) yield levels.

D. Leaching Losses

Sulfates in the soil solution are subject to leaching losses, particularly under high rainfall conditions and when soils have low adsorption capacities for this anionic form of S. The actual amounts of SO_4^{2-} leached will vary depending on soil properties, precipitation distribution patterns, and ground cover, etc. In the northeastern USA, leaching losses three to six times greater than those from crop removal have been observed. Sulfur losses by this mechanism in the Ohio River basin have been estimated to be 39 kg of S/ha per year.

E. Crop Production Systems

1. Yield Level

Whether a crop will respond to S fertilization depends on the available soil S plus inputs from the atmosphere and irrigation less the losses, usually by leaching. For example, the average alfalfa hay yield for California in 1980 was 14.3 metric tons/ha (McGregor & Heitlinger, 1980). This tonnage of hay, with an average S concentration of 0.25%, would remove 26 kg S/

ha, which is a conservative estimate. Much higher yields of 27 metric tons would remove at least 80 kg S/ha. Other high-yielding crops remove amounts of similar magnitude.

2. *Sulfur Cycling*

The S pools and flow rates from one pool to another vary from one site to another and between crops. Figure 11–6 shows an example of pasture stocked at 10 sheep/ha in New South Wales, Australia (Till & Blair, 1974). These authors and Devaud and McFarlane (1980) indicate the S cycle is practically a closed system under their environmental conditions. However, under California conditions, where most of the rain falls during the winter when plant growth is very slow, considerable available S is lost by leaching. Also, supplemental feeding is a common practice in the USA and in some Mediterranean areas (Katznelson, 1977). Allowances for these changes plus atmospheric deposition have been included in Fig. 11–6.

Another modification that should be considered is the transfer of nutrients from the pasture to resting areas. Studies with sheep in Australia indicate that 22% of the feces were deposited on 3% of the pasture area and 34% were deposited on 10% of the area (Hilder, 1964). This means that some areas of the pasture receive only a very small return of the S removed by grazing animals.

These examples demonstrate the value of S cycling studies, which can be helpful in making efficient use of fertilizers while achieving high crop production.

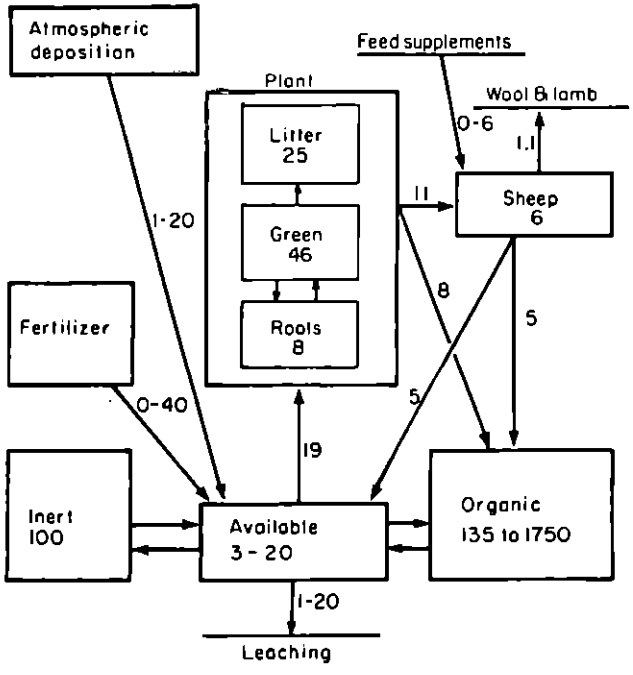

Fig. 11–6. Sulfur cycling in a pasture grazed at 10 sheep/ha. Arrows indicate flows in kilograms of S/ha per year (Till & Blair, 1974).

VII. USE OF SULFUR PRODUCTS AS SOIL AMENDMENTS

It has been known for many years that S and a number of its compounds can be used to improve calcareous and sodic soils and waters. These S-containing chemical materials include gypsum, elemental S, H_2SO_4, ammonium and calcium polysulfides, SO_2, ammonium thiosulfate, ammonium sulfate, ammonium bisulfite, and iron and aluminum sulfates. Most of these substances were described previously in this chapter.

Use of these various S materials in irrigated arid land agriculture has been reviewed by Tisdale (1970), Stroehlein et al. (1978), and Stromberg and Tisdale (1979). Brief comments will be made about the beneficial effects that these S compounds have on soils and waters.

A. Improvement of Nutrient Availability in Calcareous Soils

There are often excessive amounts of calcium carbonate in surface and subsoils in arid and semiarid regions. Land leveling for irrigation purposes may expose calcareous subsoils that are unfavorable media for optimum plant growth. Availability of P, K, B, Cu, Fe, Mn, and Zn is usually impaired by the presence of $CaCO_3$ and the associated high pH of about 8.0 to 8.2.

Table 11–12 illustrates how the productivity of a calcareous soil for growth of grain sorghum [*Sorghum bicolor* (L.) Moench] was greatly improved by the addition of either 560 kg/ha of H_2SO_4 or a similar rate of Fe in the form of $FeSO_4$.

A comparison is made in Table 11–13 of the effects of three S sources and the application of a water-soluble P fertilizer on P uptake by lettuce (*Lactuca sativa* L.) grown on four calcareous soils. It is apparent that the S treatments, especially H_2SO_4, greatly increased P uptake. Although the data are not presented here, on the average, for every 0.1 unit decrease in soil pH, available soil test P increased 3.2 mg/kg.

Another interesting example of the effect of acidification resulting from S additions on nutrient availability was reported by Hassan and Olson (1966). They applied finely divided elemental S at rates of 0, 50, 500, and

Table 11–12. Effects of $FeSO_4$ and H_2SO_4 on grain sorghum yields on a calcareous Texas soil (Mathers, 1970).†

H_2SO_4	Fe, kg/ha		
	0	112	560
	kg/ha		
0	434d*	1460bc	2275ab
112	605cd	1538ab	2474a
560	2169ab	2429ab	2230ab
5600	1885ab	1971ab	1810ab

* Yield values followed by the same letter are not significantly different at the 0.05 level.

† Standard error of the mean was 304.

Table 11-13. Average P uptake by four lettuce crops grown on four calcareous California soils (Clement, 1978).

Soil treatments	Salinas clay‡	P uptake, mg/pot† Meloland fine sandy loam§	Ripley silty clay¶	Panoche clay loam#	Treatment means
Sulfuric acid	99.5c*	103.8c	63.8cd	107.3cd	93.9cd
Soil S	83.2b	98.7c	49.0bc	85.2bc	78.9bc
Popcorn S	80.5b	77.8b	48.0b	66.2ab	58.9b
Monocalcium phosphate††	109.8c	130.7d	68.0d	129.8d	109.2d
Control	38.8a	48.8a	27.6a	39.1a	38.3a
LSD (%)	15.3	16.1	15.7	30.6	21.4

* Means in the same column that do not have a common letter are significantly different at the 0.05 level (Duncan's multiple range test).
† Uptake from S treatments averaged for two rates of 168 and 336 kg of S/ha.
‡ Fine-loamy, mixed, thermic Pachic Haploxerolls.
§ Coarse-loamy, over clayey, mixed (calcareous), hyperthermic Typic Torrifluvents.
¶ Coarse-silty, over sandy or sandy-skeletal, mixed (calcareous), hyperthermic Typic Torrifluvents.
# Fine-loamy, mixed (calcareous), thermic Typic Torriorthents.
†† Applied at a rate of 56 kg of P/ha.

5000 mg/kg to three soils ranging from acid to calcareous. These S dressings increased nutrient uptake by corn in the greenhouse as follows: P on neutral and calcareous soils, S and Mn (up to modest rates of S) on all soils, Zn in early growth stages on all soils with slight benefit extending over the late harvest on the calcareous soil, Fe on the calcareous soil, and Cu until early harvest with all soils and through late harvest with the neutral and calcareous soils.

B. Reclamation of Sodic Soils

High content of exchangeable Na^+, as in sodic soils, tends to deflocculate colloidal materials, causing soils to lose their granular structure. Such soils become almost impervious to water and air because of the loss of large pores resulting from the breakdown of soil aggregates. Root penetration is impeded, hard clods form when the soil dries, and preparation of a good seedbed becomes difficult. Surface crusting frequently results in poor germination and uneven stands.

Crop growth is reduced because of these poor physical properties. Also, the nutrition of sensitive crops such as tree fruits, vines, and some annuals will be adversely affected by exchangeable Na^+ before significant deterioration of soil physical properties has occurred. High pH values of > 8.0, which are typical of Na-affected soils, lower the availability of most plant nutrients except Mo. Typical yield reductions in sodic soils are given in Table 11–14.

Reclamation of sodic soils involves replacement of the exchangeable Na^+ with a desirable cation such as Ca^{2+}, followed by removal of the displaced Na^+ by leaching. The addition of chemicals where needed to supply

Table 11-14. Effect of exchangeable Na^+ on crop yield (Velasco, 1981).

Type of soil	Na^+	Avg decrease in crop yield
	%	
Slightly sodic	7–15	20–40
Moderately sodic	15–20	40–60
Very sodic	20–30	60–80
Extremely sodic	>30	>80

Ca^{2+} or to solubilize natural supplies of calcium carbonate and other Ca-containing minerals in soils is a common remedial treatment for reclaiming sodic soils. Sulfur and a number of its compounds are successfully used in the reclamation process.

Gypsum is an obvious choice when soils do not contain free $CaCO_3$, and it has a long history of successful use. Calcium polysulfide is another Ca-containing compound used in treatment of sodic soils.

On soils containing free $CaCO_3$, any of the acid-forming S compounds can be used to make available this natural source of Ca. Sulfuric acid added to soils will react quickly with native $CaCO_3$. When elemental S, calcium polysulfide, ammonium polysulfide, SO_2, or ammonium thiosulfate are added to soil, the S components must first be converted to H_2SO_4 by S-oxidizing microorganisms before the solubilization of soil $CaCO_3$ occurs.

A substantial reduction in exchangeable Na^+ in surface soil following the application of H_2SO_4 is shown in Fig. 11–7. Increasing amounts of leaching water also enhance the removal of exchangeable Na^+. The extent of Na^+ removal also depends on acid rates and properties of soils and waters (Miyamoto et al., 1975).

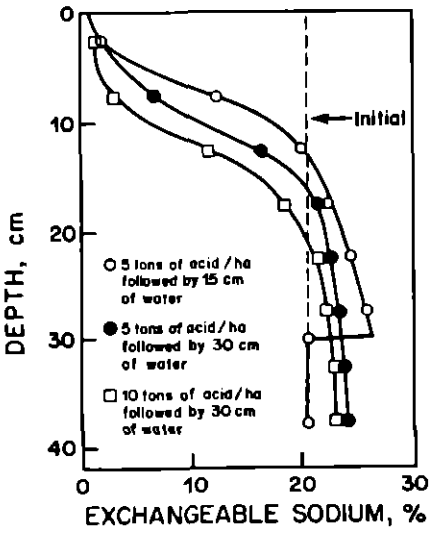

Fig. 11–7. Distribution of exchangeable Na^+ after application of H_2SO_4 and leaching water to Pima clay loam. (Stroehlein et al., 1978).

Table 11–15. Effect of surface-applied acid on the time required to pass 30 cm of water through Na-affected soils in laboratory tests (Stroehlein et al., 1978).

Soils	Na*	CEC†	Sulfuric acid, metric tons/ha‡				
			0	1	3	5	10
	%	meq/100 g	d				
Stewart clay loam (loamy, mixed, thermic, shallow Typic Durorthids)	100	45	∞	∞	>40	39	28
Pima clay loam (fine-silty, mixed [calcareous], thermic Typic Torrifluvents)	21	40	39	34	8	3	3
Gothard clay loam (fine-loamy, mixed, thermic Typic Natrargids)	17	42	8	2	1	0.6	–
McAlister loam (fine-loamy, mixed, thermic Ustollic Haplargids)	12	28	3	2	1	1	–

† CEC = cation exchange capacity.
‡ Metric tons/ha × 0.45 = U.S. tons/acre.

Soil structure improvement is important in the reclamation of Na-affected soils since structure influences the rate of water infiltration into the soil and also movement of water in the soil profile. The beneficial effect of surface-applied sulfuric acid on water infiltration rates is illustrated in Table 11–15.

There are many other dramatic examples of the ameliorating effect of S treatments on sodic soils in the USA, Spain (Velasco, 1981), and other areas of the world. For example, in some trials application of elemental S, H_2SO_4, and ammonium polysulfide to sodic soils in California, Montana, Nevada, North Dakota, and Wyoming raised crop yields between 8.5 and 400%. These and other S-containing amendments are expected to have favorable effects on crop growth on most problem sodic soils in the mountain states and in other parts of the USA and Canada (Cairns & Beaton, 1976).

C. Water Treatment

For convenience of application, gypsum, H_2SO_4, urea–H_2SO_4, SO_2, ammonium polysulfide, calcium polysulfide, ammonium thiosulfate, and ammonium bisulfite can be successfully added to arid land soils through surface-applied irrigation waters. Some of these materials are also suitable for use in sprinkler and drip irrigation systems. It has been observed that these soil-amending substances when added to water will greatly aid in maintaining water transmission properties of soils (McGeorge et al., 1956, p. 29; Howard, 1968; Robinson et al., 1968). Figure 11–8 shows how additions of gypsum and calcium polysulfide to low salt irrigation water influenced flow rates. Although each increment of gypsum improved flow rates, it took 60 mg/L or more to give a statistically significant increase in flow rate compared with no treatment of low salt water. Calcium polysulfide was also effective in improving flow rates, especially at low treatment rates. The decline in effectiveness of calcium polysulfide at the higher rates is believed to be related to the sealing of soil pores by the colloidal S that forms when polysulfide materials are placed in water.

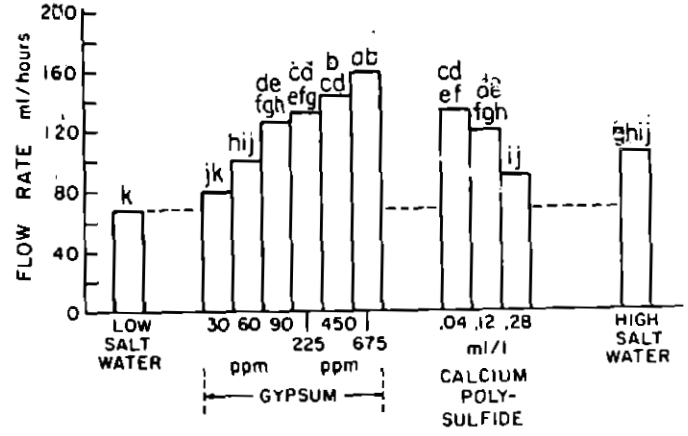

Fig. 11–8. Flow rate through Hanford (coarse-loamy, mixed, nonacid, thermic, Typic Xerothents) sandy loam with gypsum and calcium polysulfide added to low salt irrigation water (Mohammed et al., 1979).

There is still some uncertainty about the soil and water conditions under which the various amendments will have a favorable effect on water transmission properties. The most pronounced benefits are obtained with high pH and low-salt water (i.e., conductivity about 0.2 mmho and a pH > 8.4. Such water will likely contain < 20 mg/L of Ca^{2+} and be dominated by Na^+, CO_3^{2-}, and HCO_3^-. The mechanism responsible for improvement in water movement is still uncertain, but it is probably related to creating and maintaining flocculation of soil particles at the soil surface.

D. Acidification in Fertilizer Bands

In many calcareous and high pH soils, it is uneconomical to use the amounts of acidifying materials required to fully neutralize soil in the entire rooting volume. McGeorge (1945) suggested that it is not necessary to neutralize all of the soil alkalinity. More practically, soil zones favorable for root growth and nutrient uptake can be created by confining the S treatments to bands, furrows, auger holes, etc. A decline in soil pH in the vicinity of a banded mixture of ammonium thiosulfate and ammonium polyphosphate is evident in Fig. 11–9. Accompanying this soil acidification was an increase in available soil levels of Fe and Mn.

The observed benefits from banding acid-forming materials for various vegetable crops in Arizona and Colorado and for field crops in Kansas are probably the result of more favorable conditions in the zone of fertilizer placement rather than a direct nutritional benefit from S (Beaton & Fox, 1971).

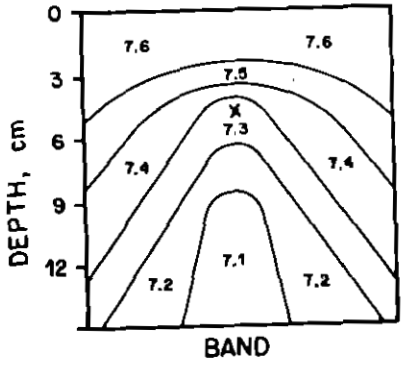

Fig. 11–9. Application of P-S solution lowers soil pH in vicinity of the fertilizer band. Point of application denoted by *X* (Leiker, 1979).

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2

Prescribing Soil and Crop Nutrient Needs

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The primary objective behind most lime and fertilizer decisions is to apply the rates of lime and fertilizer that will realize the greatest profit from the crops produced. Alternative objectives exist such as crop quality, maximum yields, soil conservation, and environmental quality. The lime and fertilizer rates necessary to meet these latter objectives may be different from those for maximum profit. To meet any of these objectives, a similar approach for prescribing nutrients can be used.

Fitts (1959) suggested that yield could be described as a function of four factors: (i) the crop grown, (ii) the soil characteristics, (iii) the climatic conditions, and (iv) the management of the producer. Other breakdowns of plant growth have been suggested, but all illustrate that many variables are involved in determining the yield potential of the crop and ultimately in making the optimum lime and fertilizer rate decisions. Some of these variables can be controlled by management, while others, such as seasonal rainfall and distribution, cannot be controlled. Because of the strong interaction between plant response to fertilizer and some of these uncontrollable factors, prescribing the exact optimum rate of lime and fertilizer prior to growing the crop is difficult. This gives added incentives for using all information available in striving to meet fertilization objectives.

The discussion in this chapter will center on soil testing for prescribing current nutrient needs and the use of soil and plant analysis to monitor the pH and fertility status of soils for adjustment of future lime and fertilizer practices.

I. SOIL ANALYSIS

A soil test program has been described by various workers as having four distinctive parts, namely, (i) sample collection, (ii) chemical analysis

of the sample, (iii) interpretation of the chemical test, and (iv) lime and fertilizer recommendations for the crop(s) to be grown. Although it is beyond the scope of this chapter to review and report all research information available, we will focus on some factors important to a sound soil test program.

A. Soil Sampling Techniques

Soil sample collection has often been described as the "weak link" in a soil test program. With the tremendous inherent variability in many soils and the additional variability caused by fertilizer and tillage practices, collection of representative soil samples is difficult. However, samples taken with proper care can be quite meaningful in making lime and fertilizer decisions.

1. Field Sampling

The objective for taking the soil sample should be considered before sampling a field. If the objective is to have an unbiased estimate of the mean fertility level of the field, then a single composite sample is justified (Cline, 1944). However, a single composite sample does not yield any information about variability within the field, which may be quite important in assessing production differences that exist between areas within the field.

A number of different sampling plans or designs have been suggested. Each has merit for particular situations. Petersen and Calvin (1965) discuss the merits of four sampling plans—judgement sampling, simple random sampling, stratified random sampling, and systematic sampling. Many sampling instructions use a combination of these sampling plans. Irrespective of what sampling technique is followed, there is unanimous agreement that a single core or shovel slice of soil is not a representative sample because of the heterogeneity that exists in most fields. However, the sampling plan must be simple and cost-effective for acceptance by those doing the sampling.

Numerous publications and soil test laboratory instructional guides exist on soil sampling. Most of these instructional guides advise that the field be divided into areas of visually uniform soil types with similar past management. They also recommend that a composite sample of 10 to 30 subsamples (cores) be taken at random over the area.

A survey was made in 1951 by the Soil Test Work Group of the National Soil and Fertilizer Research Committee on soil sampling procedures recommended by various states. A standard sampling procedure was proposed suggesting that a farm be divided into areas of uniform soil type and past management not larger than 2 to 4 ha each. If an area or a field was uniform in appearance, production, and past treatment, the sample may represent as much as 8 ha (Reed et al., 1953). These instructions are essentially those being used today by those advising farmers on proper sampling techniques. With an increase in the size of farm equipment and the concurrent increase in field size, limiting sample areas to 2 to 4 ha may not be practical. Cline (1945) suggested the minimum sample area be an area that a farmer can be expected to fertilize as a unit. In many cases it becomes the judgement of the sampler as to the number of subdivisions to make in the field.

James and Dow (1972) stated that a systematic sampling plan is superior because it provides estimates of the average soil fertility, its variability, and its distribution. Dow et al. (1973) showed that in most cases soil variation was not random and would lend itself to mapping and differential fertilization. In contrast to the above results, a systematic sampling of two 16-ha tracts of relatively uniform and nonuniform mapped soil types on 25 m grid by Illinois researchers indicated no pattern to P test values as related to a soil type or a specific area of the field (Peck & Melsted, 1973). These data illustrate that variability within a field may or may not show a consistent trend across an area. Illinois soil sampling instructions call for systematic subdividing of fields so that one composite sample is taken from every 1 to 2 ha. Five cores are suggested for the composite sample (Ill. Agron. Handb., 1982).

If the results from systematic sampling identify areas of low or high fertility, fertilizer rates can then be adjusted to the specific areas to lessen such variations and perhaps allow future sampling by a composite sample. Although detailed systematic sampling is an excellent technique, the time and expense for collection of samples will likely not be practiced except in research plots or fields being developed for production of high cash-value crops.

The ideal number of subsamples (cores) required for the composite sample to represent the sample area will depend on the nutrient being tested, soil variability within the area, sampling depth, past management, and the sampling plan being followed for the field. Statistical methods for determining the optimum number of subsamples for various sampling schemes have been published (Cline, 1944; Peterson & Calvin, 1965) and will not be presented here.

Sampling studies often reveal considerable variability among individual cores collected within a visually uniform soil area (Peck & Melsted, 1973; Hooker et al., 1976). The need for taking a sufficient number of cores for making the composite sample cannot be overemphasized. Hooker et al. (1976) found that to obtain a level of ± 3 mg/kg of soil test P, 14 to 20 cores per composite sample were required on two soil types studied. Other studies have shown that even much larger numbers of cores may be needed, depending on the soil type. The variability has also been shown to be different for various tests.

Thomas and Hanway (1968) suggested that two or more composite samples from the same area be taken as a field method for testing the adequacy of sampling. If the soil test results agree, then the area has been characterized rather well by the sampling technique used. Wide disagreement among composite samples indicates the need to reevaluate sampling, either by subdividing the sample areas or by increasing the number of cores.

More than one field should be evaluated in this manner before using the results to establish a general sampling guideline.

2. Sampling Depth

In addition to concern about variations in nutrient availability among areas of a field, the sampler should also be aware of vertical differences in nutrient availability. Most soil test development research has been done using a specific sampling depth. This makes it imperative that the sampler follow laboratory instructions on sampling depth or be able to adjust the interpretations for the altered sampling depth.

Subsoil fertility can contribute significantly to the available nutrient supply. Differences in the supply of available nutrients in subsoils may be a reflection of parent material, degree of weathering, crop rooting pattern, or restrictions in root development. Several states have classified soil types or broad soil association areas within the state as to their nutrient supply and have adjusted soil test interpretations accordingly (Schulte et al., 1980; Ill. Agron. Handb., 1982). Periodic testing of subsoils may prove to be helpful to individual producers. Additional research is needed to further define nutrient contributions by subsoils in most states.

Traditionally, suggested sampling depth on cultivated land has been the tillage depth. This has normally been a depth of 15 to 30 cm. On noncultivated land, such as pastures, a sampling depth of 5 to 15 cm has been suggested. With the rapid increase in the use of reduced or no-tillage seedbed preparation methods, a reevaluation of traditional sampling depths need to be made. However, any adjustment in traditional sampling depths must be calibrated into the interpretation of soil test results.

Greater soil test P gradients within the top 15 cm of soil have been shown on fields cropped with no-till seedbed preparation compared with more conventional methods (Welch & Fitts, 1956; Walker et al., 1970). With broadcast application of P remaining in the top 2 to 4 cm of soil with no-till planting, efficient plant utilization is a question that has not been extensively researched. Some recent research in the eastern USA suggests that P availability and utilization is quite good when broadcast on the soil surface. Kunishi et al. (1982) showed that corn made good utilization of P broadcast on no-till planted plots in Maryland, even though P remained in the top 3.75-cm layer. Broadcast P fertilizer showed little movement below 7.5 cm except at high application rates with disk and no-till seedbed preparation in Georgia (Touchton et al., 1982). Their conclusion was that P recommendations for disk and no-till systems should be based on soil samples taken from the upper 7.5 cm of soil rather than the more common 0- to 20-cm depth. In addition to concern with P accumulation within the top few centimeters of soil, a sharp decline in surface pH has been observed with no-till as compared with conventionally tilled fields (Blevins et al., 1977). This has implications for effectiveness of certain herbicides (Kells et al., 1979).

The above observations would suggest that splitting of the traditional tillage layer sample into short increments would be advantageous on fields that have been no-till farmed for several years. The results from vertical-increment sampling would reveal fields with nutrient accumulation or low pH in the top few centimeters. However, research data is needed to develop the best recommendations for succeeding crops.

Sampling depths of 60 to 120 cm are recommended by several of the Great Plains states (North Dakota, South Dakota, Nebraska, Kansas, and Oklahoma) for their available N test (nitrates). Annual rainfall in this area is normally insufficient to leach soluble nitrates below the rooting depth of most crops. In such situations, the available N test has good predictive value. Recommended sampling depth varies among states and within a state for specific crop and production practices. It would seem logical that deeper sampling would also be advantageous in testing for other soluble and mobile nutrients, such as sulfate-S. Further research is needed in this area.

3. Sampling Equipment

Sampling equipment used should provide a sample that is (i) uncontaminated, (ii) uniform in cross-section to the desired depth, and (iii) reproducible (Cline, 1944). A number of sampling tools, such as shovels, soil tubes, or augers, can meet these criteria if properly used. Welch and Fitts (1956) showed no difference in test values when sampling surface soil with a soil tube, trowel, or spade, but lower pH and organic matter results were probably due to loss of dry soil from the surface when sampling with an auger. No tool will be superior for all sampling situations.

There have been mechanical adaptations of the basic soil tubes and augers to aid in better and easier soil sampling. Hydraulic probes mounted in four-wheel drive vehicles have become quite common in the Great Plains states where sampling to depths greater than the traditional tillage layer is recommended for nitrate testing. Other types of vehicles with floatation tires can be used to transport the sampler over the field, with perhaps more representative samples being collected. However, any mechanization of sampling should be carefully examined to ascertain that the sampling objectives are realized.

4. Handling of Samples

Soil sample collection in the field should be done so that contamination does not occur from the collection container or other sources. Of special concern is contamination of the sample for micronutrient testing. If micronutrient analyses are to be performed, it is essential that all surfaces coming in contact with the soil be stainless steel, plastic, or wood, preferably in the order listed (Eik et al., 1980).

Thorough mixing of the composited cores and subsequent reduction of volume to that suggested by the testing laboratory should be done to ensure that a representative subsample is delivered to the laboratory and used in the testing. Laboratory processing of samples is geared to handle a specific volume of soil, and improper subsampling of large volume samples may lead to errors.

The sample should be handled so that minimal change occurs in the chemical or physical characteristics in the field. Ideally, testing of the soil as it exists in the field would be best. However, for ease of handling, soil samples are normally dried and pulverized by the testing laboratory before analysis. Drying of samples causes a marked change in the exchangeable K levels of many midwestern soils. The soil testing laboratory at Iowa State University had developed a system to handle moist samples (Eik et al., 1980). Immediate drying is necessary on samples analyzed for nutrients whose availability is primarily microbially related, such as nitrates. Most drying instructions suggest drying at no more than 35 to 40° C. Sample handling instructions are given by most laboratories; their instructions should be followed because their test correlation and interpretation are based on their prescribed handling of the samples.

5. Seasonal Change and Sampling Frequency

Seasonal trends in soil test values have been reported in the literature (Keough & Maples, 1972; Fitts & Nelson, 1956). Soluble salts and CO_2 may affect pH, while crop removal often affects the soil equilibria for P and K. The seasonal trend has been most consistent for K. Generally, samples taken during the growing season are lower in exchangeable K than those taken in the winter or early spring. Illinois adjusts their K soil test results on samples taken between 30 September and 1 May (Ill. Agron. Handb., 1972). In most cases, the seasonal trends have not been strong and sampling is encouraged whenever it can be done. Sampling at the same time each year would be best for research studies to assure that seasonal variation does not influence the results.

Crop removal and fertilizer additions are usually such that most routine soil test measurements do not change rapidly. Therefore, most recommendations suggest sampling every 2 to 4 yr for routine tests. The frequency of testing is adjusted in some areas by the intensity of agricultural practices and the buffering capacity of the soil. On irrigated cropland, some laboratories recommend sampling on a yearly basis.

Yearly samples taken for 2 to 3 consecutive years or multiple samples taken within a year are needed to establish the true fertility status of the area represented by the sample. This type of data base allows comparison of present and future tests to past test results in evaluating changes due to fertilization and liming. This also requires good records with field maps of areas represented by current and past samples. In the future, soil tests may be used more to monitor fertility levels in the field, making consistent sampling techniques even more important.

B. Methodology in Laboratory Operation

Variability associated with laboratory analytical tests are normally quite small when compared with field sampling variability. Most laboratories have a quality control system built into their operation. This often includes control samples that are run repeatedly in the daily operation. Several states have quality control programs to help laboratories operating in the state maintain quality control. This consists of periodically sending "check" samples to all laboratories. The question on analytical methods is more selection of the most appropriate method for the soil and climatic conditions than the analytical accuracy for the test within the laboratory.

1. Analytical Methods

The method used in the laboratory must be one that reliably measures nutrient availability in the sample. It must also lend itself to a routine soil test operation that handles a large volume of samples, and it must be inexpensive.

Discussion of individual analytical methods is beyond the scope of this chapter and the reader is referred to other references on analytical methods (Dahnke, 1980; Sabbe & Breland, 1974; Jones, 1980; Black et al., 1965; Page et al., 1982). As pointed out in these publications, modification of the method from the published procedure can alter the results, thus invalidating published interpretations. Any modification, even if slight, should be identified and thoroughly researched before incorporation into a soil test operation. Such modifications should be emphasized in publications reporting use of reference procedures.

2. Reliability of Test Methods

Technological advances in current instrumentation allows for quick and accurate detection of most essential elements. These instrumentation advancements have far exceeded the correlation and interpretation research necessary for development of a reliable soil test for several nutrients. Extreme care must be taken not to extrapolate test methods developed in one region into other regions where the need for application of the nutrient has not been documented through field research. There is also the temptation to analyze and report results for nutrients where no correlation research exists. Understanding the chemical reactions involved with a particular extraction procedure and knowledge of soil chemistry of the test area can be helpful in ascertaining the potential feasibility of the procedure. But this soil chemistry knowledge should not be the sole basis for adoption of the test method.

In addition to the capability to quickly and accurately detect most essential elements, instruments are used in testing laboratories to detect two or more elements simultaneously or in rapid succession in the same extract. This has led to research into universal extractants. Care should be taken that test accuracy is not sacrificed for laboratory convenience.

C. Correlation and Test Calibration Requirements

The native fertility of virgin soils is determined by the amount and form of nutrient elements contained in the parent material and subsequent changes by soil-forming factors, such as weathering and growth of native

vegetation. Fertility status of these virgin soils can be determined by relatively simple field experiments designed to determine which elements are inadequate. When soils have been classified into types based on parent material, texture, site characteristics, etc., fertilizer recommendations can be based on soil type and crops to be grown, using data from simple rate experiments.

After soils have been put into production, fertility status is likely to be changed by fertilization, crop removal, erosion, tillage, and other practices. Under good management and fertilizer programs, soils generally improve in fertility, while those with poor management and inadequate fertilization will likely be depleted. Since management may cause similar soils to differ greatly in fertility status, general fertilizer recommendations based on soil type may no longer be satisfactory for maximum economic returns from the use of fertilizers. Depletion and/or buildup of specific nutrients have increased the need for soil tests to determine the need for fertilization of individual fields. This is demonstrated by data from a long-term experiment in Alabama (Fig. 2–1), which shows buildup of both P and

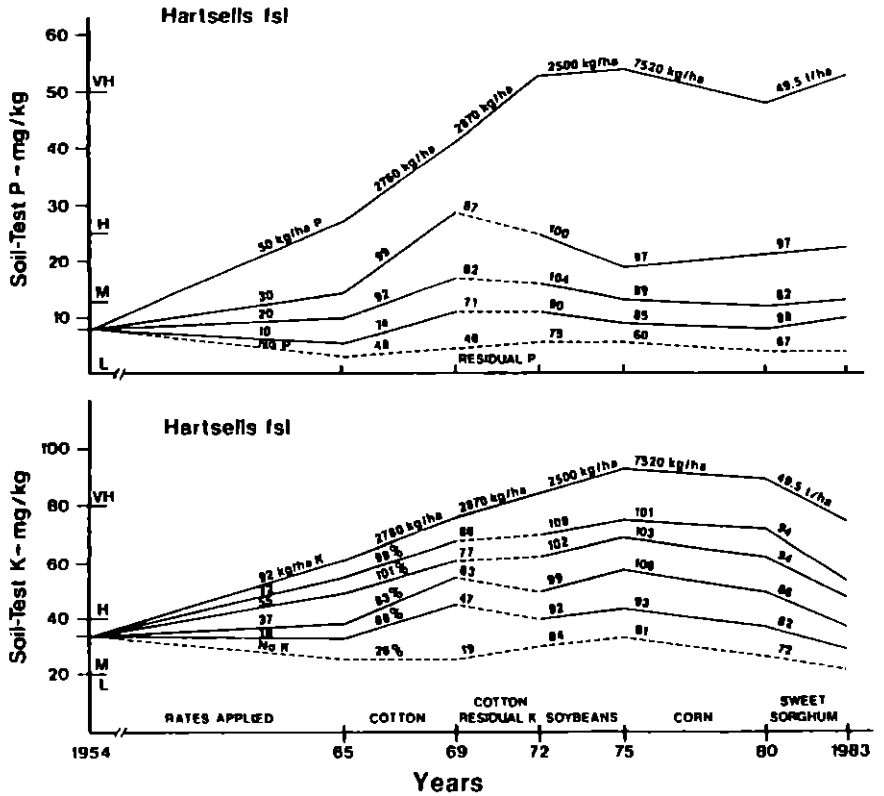

Fig. 2–1. Soil test P and K (Mehlich I) and relative yields of cotton, soybeans, corn, and sweet sorghum from 1954 through 1982 in fertilizer rates experiment on Hartsells fine sandy loam (dashed lines indicate residual period from 1970 through 1972 when none was applied). (Unpublished data.)

K on a Hartsells fine sandy loam (Typic Hapludult), with cation exchange capacity (CEC) of 6 cmol (+)/kg, from relatively low rates of fertilization applied over a 29-yr period. Data on soils over a 50-yr period showed that buildup or depletion of P and K were dependent on rates applied, but were quite consistent among these low CEC soils.

1. Collection of Data

To be useful in making fertilizer recommendations, soil tests must be calibrated against yield responses in field experiments. This calibration requires large numbers of experiments to develop reliable data on the numerous soil types and crops. Simple "some and none" experiments can be used for the purpose of determining soil test levels above which response is not expected. Such experiments can be used to determine if fertilizer is needed, but do not give much information on amounts that should be recommended. More detailed rate experiments on areas known to be deficient are necessary for determining optimum rate. Accuracy of data from rate experiments is improved by keeping plots on the same site for several crop years to permit buildup or depletion effects to be accurately expressed (Fig. 2–1).

Experiments for soil test calibration should be designed to determine the "adequate level" of a nutrient in a soil. This is the soil test level of a nutrient that is adequate for ≥ 95% of maximum yield without addition of the element. This means that crops grown on soils having this soil test level of a nutrient would not generally be expected to respond to nutrient applications. At this soil test level, some laboratories still recommend small amounts as maintenance applications; many laboratories have ceased to make maintenance recommendations, as their data show that economic returns from applications at high soil test levels are unusual.

Percentage yield or relative yield is normally used in soil test calibration research for plotting data from numerous experiments conducted on different soils to normalize for individual location effects. Soils vary widely in soil test levels required for adequacy and should be grouped into categories showing similar response. Such groupings may be based on CEC or on soil associations such as Coastal Plain or Piedmont soil regions, which would serve the same purpose. Crops also vary in fertility requirements, so experiments should be conducted with as many crops as possible so that crops can be grouped according to response characteristics. This is demonstrated in Fig. 2–1, where relative yields of cotton can be compared with those of soybeans, corn, and sorghum, where P or K is deficient.

2. Calibration Experiments

Initial calibration can best be accomplished using large numbers of simple experiments on soils covering a range of fertility levels. Only two rates of a nutrient are required to determine if a soil will respond, but four or more rates are generally needed to determine the optimum amount needed on responsive soils. Experiments should include rates of all nutri-

ents suspected to be deficient. This can be determined by soil tests prior to site selection. Prior to the establishment of experiments, soil samples should be taken from at least each replication to determine within-site variation.

Selection of treatments should begin with a standard treatment including what is considered to be adequate amounts of all applied nutrients. Yield from this treatment is assigned a value of 100% and yields from other treatments are expressed as percentages of this treatment. Response to other nutrients is determined by omitting one at a time, while applying adequate amounts of other nutrients that may be deficient. Several rates of a nutrient may be used, but other practices, including the use of lime or micronutrients, should be constant and adequate. Such experiments do not require an unfertilized check, because the law of the minimum makes it impossible to accurately determine the need for one nutrient when another is limiting the yield. Field experiments of this type are seldom precise enough to accurately determine interactions among nutrients where more than one is limiting. When yields are seriously limited by drought, poor stands, or other uncontrolled factors, data should not be used in calibration.

3. *Statistical Methods*

Randomized block designs with three to five replications have been used most frequently in calibration work with large numbers of simple experiments on similar soils at different sites. Many procedures have been reported for analyzing and partitioning data for use in calibration. Many response equations have been developed, but few have been used extensively in making fertilizer recommendations from soil tests. Detailed calculations for making recommendations for individual sites are generally not justified because the entire process of making fertilizer recommendations from soil tests involves a series of approximations. These include sampling variation in the field; analytical variation in the laboratory, which is generally much less; experimental variation incurred in field calibration experiments; variation in yield level and response among experiments on different soils grouped together; variation among crops in fertility requirements; and safety factors associated with suggested use of higher fertilizer rates than that shown to be needed by research data. Farmers frequently increase applications above recommended rates because of inaccuracy in application rates and/or to compensate again for the factors above. Even with all of these limitations, a good soil test recommendation program is the best and most reliable basis for determining fertilizer needs.

Perhaps the most frequently used calibration procedure is demonstrated in Fig. 2–2, where each point plotted represents one experiment. Regression curves from such data may be calculated as described by Bray (1948), Melsted and Peck (1977), and others. Cate and Nelson (1971), Fitts and Hanway (1971), and Nelson and Anderson (1977) described a simplified system for partitioning data based on probability of response. This system lacks precise definition for the "critical level" which may be needed in making recommendations. Hauser (1973) points out that in many cases

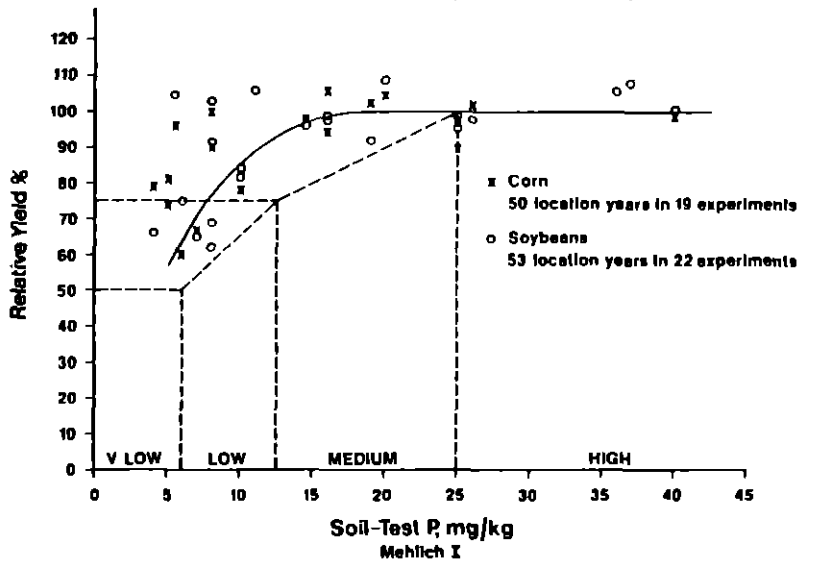

Fig. 2–2. Relationship between soil test P and relative yields of corn and soybeans on low CEC soils in Alabama, 1976–1981. (Unpublished data.)

hand-drawn curves may be adequate. These can be fitted into a system such as described by Cope and Rouse (1973), where the curve is divided into sections based on definitions of soil test ratings for percentage crop yields predicted from the curve (Fig. 2–2). Percent yield refers to that yield from plots receiving none of the nutrient, relative to that from an adequate supply, while other nutrients and inputs are optimum. The points plotted in Fig. 2–2 are in most cases 2- to 5-yr averages from long-term experiments where soil test levels of check plots were well established and quite stable. About two-thirds of these plots had not received P applications for 25 yr. The solid line curve was hand-drawn through the data points. The dashed line is the interpretation now in use in the Auburn University Soil Testing Laboratory on which P recommendations are based for corn and soybeans. These recent yield data show that very little response was obtained on "medium" fertility level soils in these long-term experiments. The discrepancy between the two curves shows that present P recommendations are more than adequate. These data indicate that a large safety factor is built into this system and that consideration should be given to lowering soil test levels required for "medium" and "high" ratings. The data suggest a need for constant and continued updating of calibration programs that are based on old data. New experiments should be conducted to keep calibration current with increasing yield levels and changes in prices of fertilizer and crops produced.

4. *Greenhouse Studies*

Greenhouse studies are useful in comparing soils and evaluating their relative nutrient-supplying capacity by growing plants in the same environ-

ment, except for soil differences. Total nutrient uptake can be measured by analyzing plant materials. Different extractants can be compared by determining correlation between amounts of nutrients extracted and nutrient uptake. This can often be done more quickly and accurately in the greenhouse than in field experiments. Data from greenhouse experiments are of limited value in calibrating nutrient test levels for fertilizer recommendations. These calibrations must be conducted in field experiments, but greenhouse and laboratory studies can be helpful in locating field experiments on soils that are likely to be responsive.

D. Recommendation Philosophy

The primary objective of a soil testing program should be to make lime and fertilizer recommendations that will produce maximum economic returns. This involves consideration of many factors that contribute to production of profitable yields. Various laboratories use widely different procedures and philosophies in arriving at recommendations. Their effectiveness and reliability should be judged on the accuracy of the recommendation in producing economic returns rather than on how it is reached. Profits are reduced by use of fertilizer in excess of optimum rates, but this loss is generally less than that from insufficient fertilizer applications. Growers can use either insufficient or excessive amounts of most nutrients for several years without being conscious of economic loss. Growers and fertilizer suppliers, using laboratories that recommend excessive rates, will be satisfied until research is done to determine soil tests levels and fertilizer rates associated with maximum economic returns (Olson et al., 1982).

1. Nutrient Accumulation and Removal

Increases in soil test P levels in the plow layer of some fertilized soils have been generally recognized for many years. Because P is not leached by passage of water through the soil, application of rates higher than amounts removed in harvested portions of crops results in P accumulation. The P content of most crops is usually in the range of 0.2 to 0.4%, so that 1000 kg of dry plant material contains only 2 to 4 kg of P. On the other hand, removal of K may be much greater when all of the plant material is removed, often being as high as 2 to 4% in nongrain portions of many crops. Potassium is subject to some leaching, particularly on extremely sandy soils. Cope (1981) reported that on six soils in Alabama over the 50-yr period 1928–1978, average annual application of 14 to 18 kg/ha P increased soil test P from an average of 19 mg/kg in 1928 to 33 mg/kg by 1957. Application of 28 kg/ha K over the 50 yr in a cotton-corn rotation produced top yields and increased the level of soil test K in five of the six soils.

Research data and soil test summaries from many states have shown increasing levels of both P and K under current fertilizer practices. Regular soil testing by reliable laboratories will promote efficient use of fertilizer and increase profits. Rates of P and K that produce maximum returns have been shown to also increase soil test levels. Therefore, recommendations

may be limited to rates from which response can be predicted on the next crop or within the rotation. As long as the release rate of a nutrient from the soil is adequate to supply the needs of a crop without reduction in yield or quality, application of the nutrient is not justified.

2. Cation Ratio vs. Sufficiency Levels in Making Recommendations

Soils vary tremendously in their capacity to supply P and K to growing crops. Some of the factors that affect the nutrient-supplying capacity of soils are amount and type of clay, organic matter content, total nutrient content, and amounts of extractable nutrient ions. Soils with similar amounts of chemically extractable P or K may vary widely in nutrient-supplying capacity to crops. Therefore, these differences in supplying power and response characteristics must be considered in making soil fertility ratings and recommendations based on soil tests.

McLean (1977) described two concepts of soil test interpretation that have been widely used. These are the sufficiency levels of available nutrients (SLAN) and basic cation saturation ratio (BCSR) methods. The SLAN concept involves assigning soil test sufficiency levels based on response data from field experiments. This concept is illustrated by Fig. 2–2 and is sometimes referred to as "fertilizing the crop." Most laboratories using this interpretation concept adjust sufficiency levels for crop and soil association effects. This concept assumes little or no interaction among nutrients in their effect on needed fertilization and applies to all nutrients.

The BCSR concept is used by many commercial laboratories to adjust for interactions among cations so that a specific cation ratio or base saturation is achieved. This involves determining the CEC and making recommendations to achieve specific ratios among K, Mg, and Ca ions in the soil. Recent research reported by McLean (1981) and others has shown that the values for BCSR per se are completely independent of crop yields. Use of this concept results in recommendations that are higher than can be justified by most recent studies.

Some state laboratories have also recognized a need for classifying soils into groups for making P recommendations. Soils with low CEC release P more readily to extracting solutions and therefore require higher levels for adequacy than do soils with more clay or organic matter. Laboratories in Alabama, Georgia, Florida, and South Carolina separate the sandy soils of the Coastal Plain from those of the Piedmont or others that have more clay or organic matter. This relationship for P is reversed from that with the cations as indicated by Cope and Rouse (1973).

3. Reporting Results and Making Recommendations

Many systems of reporting soil test results to growers are used. Most laboratories use interpretive ratings ranging from very low to very high to identify the level of sufficiency in the soil. These ratings are generally based on anticipated yield without application of the element. High and very high are usually above the adequate level. Many laboratories recommend maintenance applications at these levels, but some are discontinuing this prac-

tice as research data show that they are generally not needed. Medium is normally the area of moderate response and low or very low is where response should be expected. The recommended rate of application to obtain optimum yields at these soil test levels will result in a gradual soil test increase.

Most laboratories recognize differences among crops in their fertility requirements. Some laboratories rate soils differently based on crops to be grown, such as vegetable and other horticultural crops; forage crops, which remove large amounts of nutrients; cotton; and crops grown for silage, which have higher requirements for P and K than do corn for grain, rice, most other grasses, and peanuts (Cope et al., 1981). These crops with low P and K requirements can frequently be grown without direct applications when grown in rotation with other well-fertilized crops.

In addition to ratings, most laboratories use some method of reporting results more precisely, especially for use in record keeping and fertility monitoring by growers. Some report kilograms per hectare or parts per million extracted, but these data are often confusing to growers, because each element has a different level for a specific degree of adequacy. For example, the adequate or critical level for one soil may be 25 mg/kg P, 120 mg/kg K, 200 mg/kg Ca, and 30 mg/kg Mg. Adequate levels in other soils and from other extracting procedures would likely be different for each element.

To simplify reporting and make it more easily understood by growers, some laboratories have developed fertility indexes for use on soil test reports. Use of computers in making soil test recommendations has simplified reporting of index values. No indexing system has been universally accepted. Some form of a percent sufficiency index, as reported by Cope and Rouse (1973), offers promise of simplified reporting and record keeping. This system assigns the adequate level of each element for each soil a value of 100. Below this level the index follows the yield curve and above is a straight line relationship. It has been particularly helpful in emphasizing to growers the degree of buildup of P under continued applications.

II. PLANT ANALYSIS

Plant analysis, like soil tests, can be a valuable aid to producers in making efficient use of lime and fertilizer. Recommendations based on soil tests are made prior to seeding; however, plant samples for analysis cannot be taken until the corp is growing, resulting in a delay that may prevent corrective action for the current crop. The value of plant analysis may therefore be more for the future than for current crops, especially for annual crops.

According to Ulrich and Hills (1967), *plant analysis* is defined as "the concept that the concentration of a nutrient within the plant at any particular time is an integrated value of all the factors that have influenced the nutrient concentration up to the time the plant sample is taken." Plant tissue can be analyzed for the total quantity of the nutrient or for only a soluble fraction of the nutrient in the plant sap. The latter is commonly referred to as tissue testing and normally measurements are taken in the field for only N, P, and K in freshly extracted plant sap. Our discussion will focus on plant analysis for total quantity of nutrient present in the plant; however, much of the information on sampling and interpretation also applies to tissue testing.

A plant analysis program can be thought of as having four parts: (i) collection of the sample in the field, (ii) chemical analysis of the plant tissue, (iii) interpretation of the analytical results, and (iv) recommendations based on the interpretation and supplemental information provided with the sample. Our discussion will center on these four factors.

A. Plant Sampling Techniques

Collection of proper plant tissue samples is essential to a sound plant analysis program. Not only do we have to concern ourselves with field division and sample handling in plant analysis, but we must also concern ourselves with which part of the plant and at what growth stage to sample.

1. Field Division

Research information is limited on methods of subdividing fields for collection of plant samples. Likewise, little research is reported on the sampling pattern to follow in the field. The purpose for sampling will influence the choice of sampling procedure. Plant samples are normally taken either to monitor the nutrient status of the crop or to help diagnose poor growth. Our discussion on field division will relate to these two objectives for sampling.

Field division and sampling patterns to monitor nutrient status of a crop should be similar to those used for soil sampling in the field. This allows the information from the soil and plant analysis to be used in combination for a better interpretation. The person taking the plant samples should be alert for abnormal growth areas that were not apparent when soil sampling. If soil samples were not recently collected from the field, then they should be taken at the same time as the plant samples. For the diagnostic approach to plant analysis, normal and abnormal growth areas should be sampled separately for comparison of results.

The sampler for both approaches should avoid plants of different maturity due to planting date differences that might exist within the field. Likewise, sample each cultivar separately if several have been planted in the field to avoid differences in test results due to genetics. A separate composite sample should be taken from different maturity or cultivar areas to minimize plant size and maturity effects (Jones & Steyn, 1973). As with soil sample collection, avoid unusual soil areas when plant sampling to monitor overall nutrient status of the field. The number of subsamples required to characterize the field will vary with crop and soil conditions. In general, the larger the number of subsamples composited, the more likely the test sample will reflect the condition in the sampled area.